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PROCEEDINGS OF THE 13th COTTON UTILIZATION RESEARCH CONFERENCE,

New Orleans, La., May 14-16, 1973

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FOREWORD

The 13th Cotton Utilization Research Conference was held in New Orleans, La., May 14–16, 1973. This is an annual conference sponsored by the Southern Regional Research Center to report progress in cotton research during the year. It also provides a medium for the exchange of information between the textile and related industries and the Government, with the aim of improving research.

Studies conducted on cotton products, including chemical finishes and improvements in the mechanical processing of cotton fibers, were presented. Progress was reported on durable press, cotton/polyester blends, and knitted yarns and fabrics. Particular emphasis was on flame-retardant treatments for textiles.

G. E. GOHEEN, *Acting Area Director,*
Southern Regional Research Center

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ELECTRON DIFFRACTION STUDY OF CELLULOSE

By Jacques J. Hebert and Linda L. Muller[1]

(Presented by Jacques J. Hebert)

Cellulose, the most abundant polymer, constitutes the cell wall of most, if not all, green plants. In the form of wood, wood pulp, and cotton, cellulose represents a very valuable agricultural commodity and is, therefore, the subject of much research. Chemical modifications of cotton are brought about predominately by the reaction of various reagents upon the surface of the crystalline elementary fibrils that make up the subfiber structure. For this reason, electron-diffraction studies were undertaken to evaluate this microstructure and its various modifications. Electron-diffraction techniques offer several advantages over X-ray methods. Electrons have more interaction with matter than X-rays and are scattered with more intensity; therefore, much smaller samples can be used.

Samples of pure cellulose from four sources (ramie, cotton, *Valonia*, bacteria) were used in the investigation of unit cell dimensions. Fibers of each sample were beaten in water with a laboratory blender. Droplets of the cellulose-water slurry were placed upon uncoated 500-mesh copper grids and cooled in an electron microscope to —100° C before diffraction analysis. Patterns were recorded on glass photographic plates to eliminate distortions owing to film shrinkage, and each specimen received approximately equal electron dosages.

Results of this experiment indicate that the unit cell dimensions of cotton and ramie are quite similar and that the reflections in their respective patterns could be indexed by the normally accepted monoclinic unit cell of cellulose I. Cellulose from *Valonia* and the bacteria, however, exhibited certain reflections in their diagrams that could not be indexed by this cell but could be indexed by a cell having the *a*- and *c*-axes twice as long as those of the normal cell. These results seem to verify the existence of at least two crystalline polymorphs of cellulose I, cotton and ramie having one structure and *Valonia* and bacterial cellulose having another.

In a study of the modification of the crystal lattice of cellulose during the mercerization process, samples of purified cotton fibers were treated with a 4 *N* solution of sodium hydroxide before fragmentation. X-ray diffraction tracings indicated that substantial conversion to a cellulose II lattice had taken place. The electron diffraction diagrams, which involved only small samples, clearly illustrated mixed patterns of cellulose I and celulose II lattices. Only after increasing the concentration to 11 *N* was the lattice conversion complete in a single treatment. Conversion of the lattice with more dilute solutions required multiple treatments separated by a complete washing and drying procedure.

Since crystallite orientation affects the ultimate strength of the fiber aggregates, electron diffraction techniques were employed to study this orientation among various cotton fibers and to trace its modification during swelling and under tensile stress conditions. Swelling in a 4 *N* solution of sodium hydroxide brought about a marked disorientation within the crystallites; however, when tension was applied to swollen fibers, the crystallite orientation was improved considerably. It is believed that this improvement in orientation and the lattice conversion are the sources of the increased strength obtained by mercerization under tension.

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A RADIAL-STRAIN TESTER FOR MEASURING STRESS-STRAIN BEHAVIOR OF LOW-MODULUS TEXTILES

By Charles B. Hassenboehler, Jr.,[1] Mary L. Nelson,[1] Louis C. Weiss,[1] and Thomas Taggart[2]

(Presented by Charles B. Hassenboehler, Jr.)

The radial-strain tester (RST), a simple device for determining stress-strain behavior of low-modulus materials, such as knitted textiles, under uniform biaxial strain is described. In biaxial testing, the test specimen is physically subjected to strain in two principal directions in the plane of the fabric. In the Mullen diaphragm tester and the recently introduced Celanese bagging test, the specimen perimeter is fixed while the central area is deformed out of the fabric plane, and the strain is a function of the radius along the specimen. In larger diaphragm testers, the specimen is usually deformed into a spheroidal shape, and the stress at any point is dependent on the shape of the surface at that point. For the diaphragm tester, the biaxial stress ratio at any point is unity. Other biaxial testers, not used in routine testing of textiles, produce a constant ratio and magnitude of biaxial strain throughout a known region of the specimen.

The radial-strain tester is an expandable circular pin frame that expands the circumference of the sample in the plane of the fabric, and records the cumulative stress-strain curve through a standard Instron tensile tester. The RST fixture was designed to measure the elastic behavior of textiles due to strains approximating those which occur in the back, seat, and knee stretch of garments. Radial or uniform biaxial deformation is of specific interest in testing the effects of treatments on knitted materials because it minimizes yarn-loop sliding during testing. Figure 1 depicts the expandable circular pin-frame jaw that stretches the specimen radially.

Figure 2 depicts a segment of a circular specimen during planar expansion of the circle, with geometric quantities used in the equations. The geometry shows that the strain in the radius (ε_r) is equal to the strain in the chord (ε_c). Since this holds for any angle α, it follows that uniform planar strain is produced by radially expanding the circumference of a circular sample. Ideal radial strain throughout the specimen is only approximated with this RST since continuous gripping of the circumference is not realized. An edge effect occurs, as is shown in figure 3.

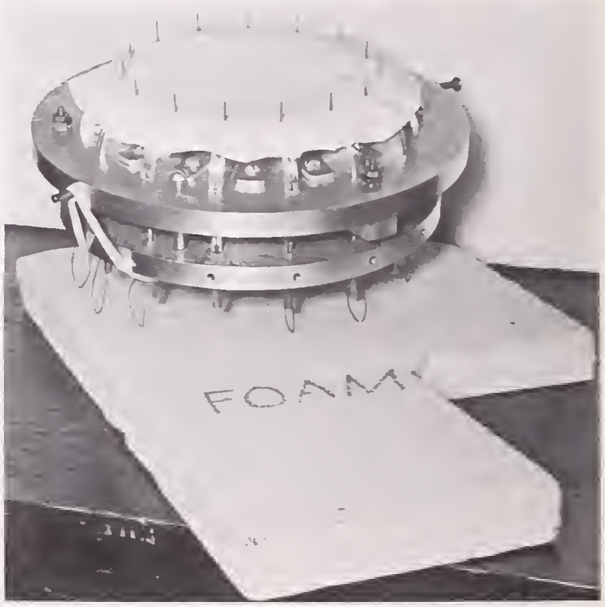

FIGURE 1.—Inverted RST with specimen mounted on pins.

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Figure 4 is a schematic drawing of a cross section of one stretching unit of the instrument. Fifteen such pulleys, equally spaced, and equidistant from the center line C–C, are built into the circular plate B. The pin D is one vertex of a 15-sided regular polygon approximating a circle 4½ inches in diameter. The force on each pin is transmitted to the cable plate E, which fastens to the Instron load cell. The load cell records a cumulative force. The increase in radius of the fabric circle is equal to the increase in separation of plates B and E due to the crosshead movement.

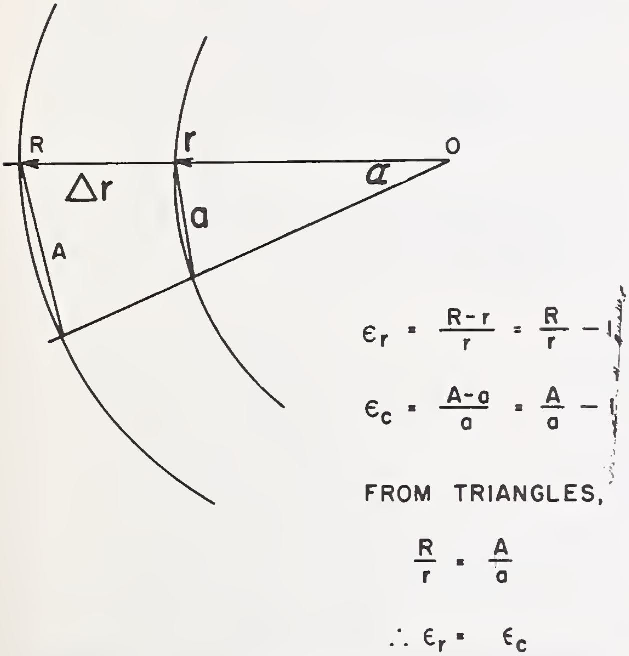
R
r
O
Δr
α
a
A
$\epsilon_r = \frac{R-r}{r} = \frac{R}{r} - 1$
$\epsilon_c = \frac{A-a}{a} = \frac{A}{a} - 1$
FROM TRIANGLES,
$\frac{R}{r} = \frac{A}{a}$
$\therefore \epsilon_r = \epsilon_c$

FIGURE 2.—Segment of circular specimen under radial expansion.

Although the pins of the device diverge so as to subject the specimen to a definite biaxial-strain ratio of unity, knits are not always deformed as such because edge effects about the pins can be unequal on anisotropic media. Edge-effect inequalities can be diminished greatly by increasing the number of pins around the pin frame jaw.

Extensometer measurements showed that the strain along the bias of a specimen was directly proportional to the increase in diameter of the pin frame over the entire strain range. The proportionality constant was three-fourths for the cotton knits tested.

Three patterned, 100%-cotton jersey knits of fancy construction were tested: a cobblestitch and a honeycomb knit of equal weights, and a lightweight honeycomb. All were relaxed by three cycles of machine washing and tumble drying. Portions of the samples were given a durable-press treatment of 5% dimethyloldihydroxyethyleneurea (DMDHEU) with a pad-dry-cure procedure. Circular specimens, six inches in diameter, were mounted on the RST by placing each specimen on a flat, foamed, polystyrene board, sticking the exposed pins of the device through the relaxed specimen into the board, and

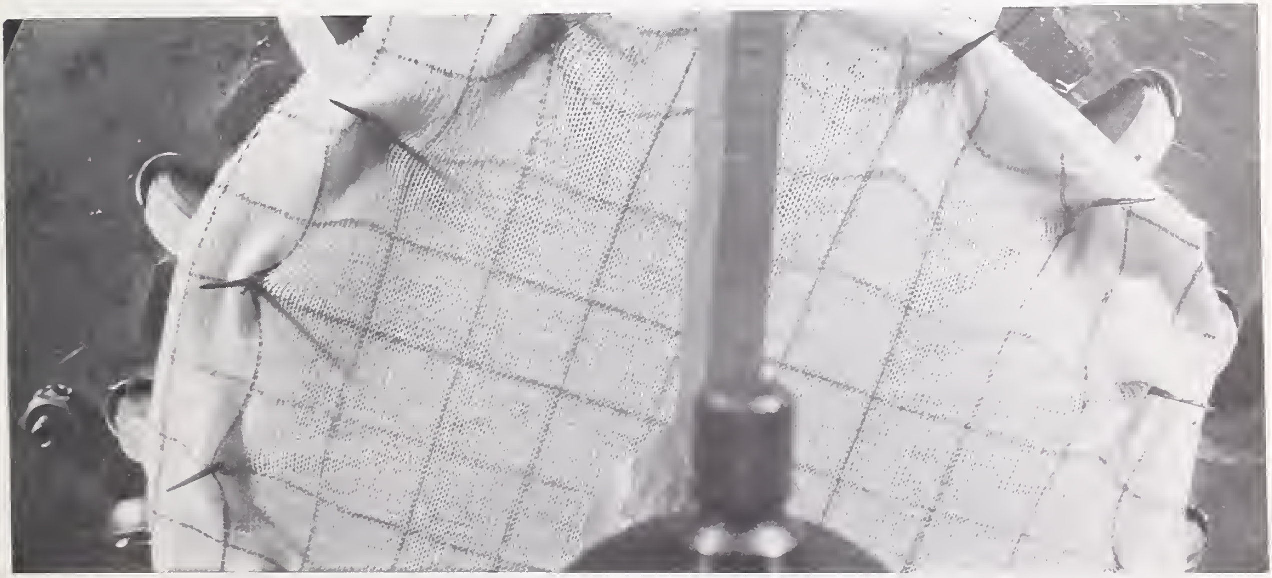

FIGURE 3.—Cotton knit under strain in tester, showing edge effects.

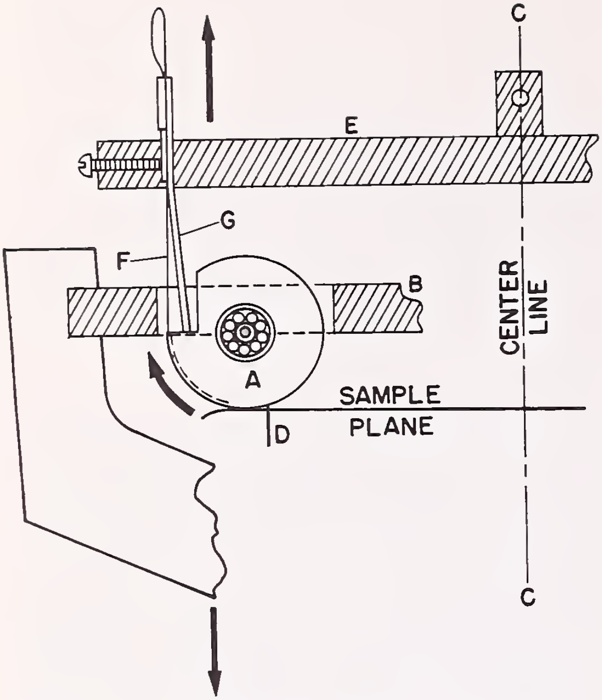

FIGURE 4.—Cross section of a unit of the RST in its initial position.

then removing the foam board. The assembly shown in figure 1 was then fitted into the Instron for testing. This method allows the fabric to be easily mounted on the tester pins or jaw in a relaxed condition without wrinkles.

A radial strain of 1% means that the diameter of the circle of pins increased by 1%. The test specimens were subjected to a strain rate of 22.2% per minute. In the recovery tests, the specimens were strained to a prescribed level, then returned immediately at six times the operating strain rate. After the relaxation period, the specimen was cycled to the next strain level. The set was determined from characteristic sections of the curve at which the specimen visibly flattened out.

Figure 5 shows specimen variation in the force-deformation curves for the three control samples. Low variability is shown by the nearly coincident curves for the specimens of each sample. The weight of the fabric had a greater influence on stress-strain behavior in these three cotton knits than differences in construction.

The effect of relaxation time on residual set was investigated briefly. Figure 6 shows the residual set in the durable-press-treated honeycomb fabric and its untreated control. At machine radial strains of up to 20% (or fabric radial strains up to 15%), the treated honeycomb showed an improvement in its recovery after the longer relaxation time. The recovery values are based on the recovery of the entire specimen within the jaw.

Figure 7 gives the residual set versus strain level for the three durable-press-treated cotton knits and their controls. The order of recovery for the untreated knits is related to the magnitude of the cumulative force to which the sample was subjected in attaining a given strain, as in

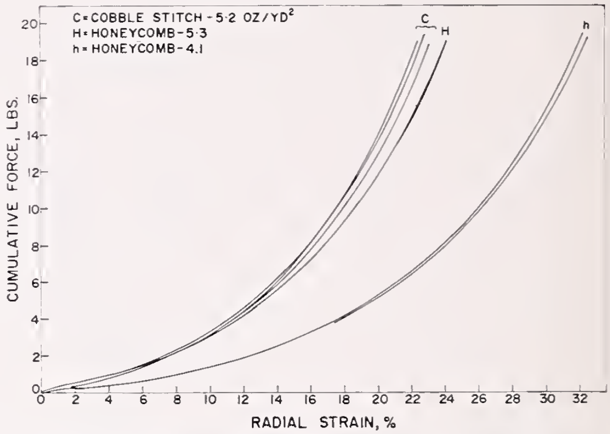

FIGURE 5.—Force-deformation behavior of cotton jersey knits; duplicate and triplicate curves show specimen variation.

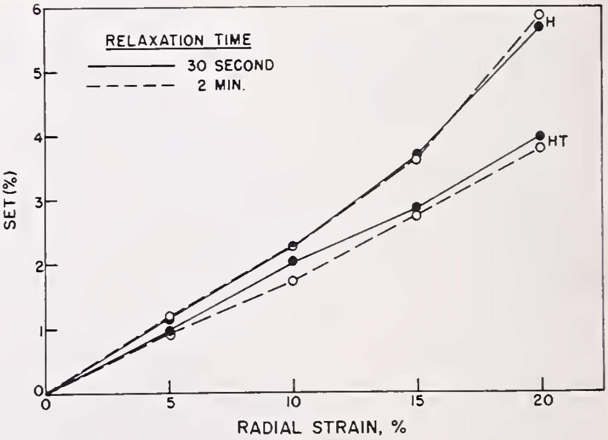

FIGURE 6.—Plot showing effect of relaxation time on residual set for cotton honeycomb knit (H) and the durable-press treated honeycomb (HT) after 0.5 min (solid lines) and 2 min (broken lines) of relaxation.

figure 5; that is, the lightweight honeycomb (h) required the least stress to stretch it to a given strain level, and its residual set is least.

The design of the instrument lends itself to several interesting mechanical variations. The pulleys of the apparatus can be arranged in an elliptical configuration in order to subject a textile to a different ratio of biaxial strain for special-purpose testing. Alternatively, the directional forces around the specimen can be measured by use of an equilibrium-ring strain gage connected to the cable ends.

The value of the RST as an instrument for routine testing is enhanced by the unique state of strain it produces, and the simplicity with which it is produced. Further work is needed to establish the practical value of this mode of strain in predicting end-use properties of various textiles.

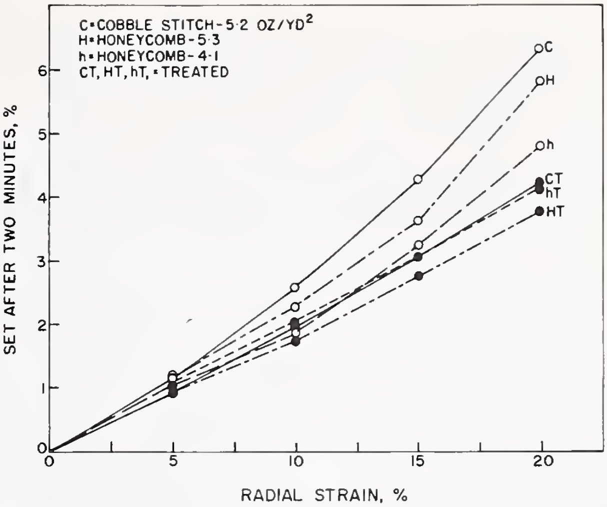

FIGURE 7.—Residual set versus strain for cotton knits of different weight and construction.

PHOTOFINISHING FOR COTTON TEXTILES

By Jett C. Arthur, Jr.[1]

In this study of photofinishing for cotton textiles, when cotton was irradiated with ultraviolet light, oxidative reactions began and cellulosic free radicals were formed. Free radicals were formed in dried, purified cotton irradiated with near-ultraviolet light that had wavelengths of about 3,250 to 4,000 A. The maximum concentration of free radicals was observed on irradiation of cotton with near-ultraviolet light that had a wavelength of about 3,600 A. The electron-spin resonance spectrum of the cellulosic radical had a line width of 8–10 gauss and a g-value of 2.0045. There are two possible explanations for the process that led to the formation of free radicals in cotton irradiated with light. First, the light is absorbed by a specific chromophore. In this case there should be homolytic bond scission and a direct correlation between formation of radicals and oxidative degradation of the cellulosic molecule. Second, the light is absorbed by an electron band structure. In this case an intermediate state should be produced with the electrons in an excited state and extremely mobile in this semiconductor model.

Near-ultraviolet light with a wavelength of 3,600 A would correspond to an energy of about 3.4 eV or 80 kcal/mol. Homolytic scission of either C—C or C—O bonds would require an energy of 80 to 90 kcal/mol; cleavage of a hydrogen atom from cellulose would require about 100 kcal/mol. Near-ultraviolet light (3,600 A) would only marginally meet the energetic requirements for homolytic bond scission. Absorption of near-ultraviolet light by a specific chromophore and homolytic bond scission of cellulose were not completely ruled out. However, the principal process that led to the formation of the maximum concentration of free radicals in cotton on irradiation with near-ultraviolet light evidently depended on absorption of light by an electron band structure. Also, oxidative degradation of cotton irradiated with near-ultraviolet light was low compared to degradation of cotton irradiated with far-ultraviolet light (2,537 A). Therefore, near-ultraviolet light was used in the development of a photofinishing process for cotton textiles that involved free radical initiation.

Electron-spin resonance spectra of free radical intermediates formed during photoinitiated graft polymerization reactions of vinyl monomers onto purified cotton cellulose were recorded. Photolyzed solutions of vinyl monomers, in the absence of cellulose, did not generate electron-spin resonance radicals. Evidently, the cellulose radical formed on photolysis added to the double bond of the vinyl monomer to yield propagating radicals, as follows:

$$cell\text{-}H \xrightarrow{h\nu} cell\cdot + \cdot H \qquad (1)$$

$$cell\cdot + nM \rightarrow cell\text{-}(M)_{n-1}M\cdot \qquad (2)$$

Cell-H represents the cellulose molecule; *cell·*, the cellulose radical; *M*, monomer; and *M·*, monomer radical. Typical electron-spin resonance spectra for propagating radicals included poly(acrylamide), three lines, 0, ±22 gauss; poly(methacrylamide), five lines, 0, ±22, ±44 gauss; and poly(diacetone acrylamide), two lines, ±11 gauss.

The rates of photopolymerization of selected vinyl monomers from water solutions with cotton were as follows: diacetone acrylamide>acrylamide, methacrylamide>N,N-methylenebisacrylamide. Infrared spectra of the copolymer products showed increased carbonyl group absorption. The cotton-poly(acrylamide) and the cotton-poly(diacetone acrylamide) copolymer products were stable to solvent extraction and to acid hydrolysis, but only the latter was stable to base hydrolysis. Differential dyeing indicated variation in the deposition of the polymers within the fabric structure. Large increases were observed in the moisture regains of cotton-poly (*N*,*N*-methylenebisacrylamide) and cotton-poly-(methacrylamide) fabric copolymers, as compared with cotton fabric controls. The fabric copolymers had elongations at break slightly greater than that of untreated cotton and retained about 90% of the breaking strength and 70% of the tearing strength of untreated cotton.

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Acrylated and methacrylated cotton fabrics that had been irradiated by near-ultraviolet light in nitrogen had increased wrinkle-recovery angles, as compared with those of control fabrics. The wrinkle-recovery angles of the photolyzed fabrics were dependent on degree of substitution of the chemically modified fabrics. For example, after 60 minutes of photolysis of the fabrics wet with *N*,*N*-dimethylformamide, acrylated fabrics with degrees of substitution ranging from 0 to 0.5 had wrinkle-recovery angles (wet) ranging from 182° to 296°; photolyzed methacrylated fabrics with degrees of substitution ranging from 0 to 0.36 had wrinkle-recovery angles (wet) ranging from 185° to 291°. The breaking strengths of the fabrics were decreased during chemical modification; however, these properties were not further changed during photolysis.

The possible development of a photofinishing process for cotton textiles that combines both graft polymerization reactions of vinyl monomers with cotton and cross-linking of chemically modified cotton was suggested.

POTENTIALS OF ORGANIC SOLVENTS IN FINISHING OF COTTONS

By D. M. Soignet, R. J. Berni, M. W. Pilkington, and R. R. Benerito[1]

(Presented by D. M. Soignet)

Early work in the physical chemical group at Southern Regional Research Center focused on solvent processing of textiles as a means of increasing ionic sites on the cellulose matrix of cotton. Emphasis was on the preparation of sodium cellulosate in nonaqueous media and its use with a variety of finishing reagents capable of reacting with cellulosate ions.[2] We were successful in increasing the degree of substitution of diethylaminoethyl, quaternary base-, carboxymethyl, and sulfonoethyl groups on cotton by the use of nonaqueous solvents. These ionic sites, as well as original cellulosate sites, were used to catalyze subsequent reactions of cellulosic hydroxyls with conventional finishing reagents. In particular, cottons with in situ reaction sites were reacted with dimethylolated ureas or with difunctional epoxides to produce durable-press (DP) cotton in nonaqueous media. Acid salts of DEAE cottons that dissociated on heating were effective in delayed cure processes for producing DP cottons by conventional aqueous methods. Of particular interest was the production of DP cottons containing quaternary base groups capable of attracting fluorescent dyes or whitening reagents. Also of interest were DP cottons containing acidic groups of various acid strengths that might act as dye assists, soil-releasing reagents, or active sites for subsequent cellulose modifications.

Interest has continued in developing novel processes for finishing cottons in organic solvents and in the application of such systems to the finishing of cotton and polyester blends. Particularly with blends is the presence of active ionic sites important to uniform finishing treatment. Polyfunctional epoxides, many of which react too readily with water, and some of which are only partially soluble in water, were used to finish cotton and cotton-polyester blends in nonaqueous media. In addition, attempts were made to produce DP cottons by reacting fabric with methyl ethers of dimethylolated ureas or carbamates in organic solvents. Because of poor reactivity of these ethers in the absence of water, the dimethylolated ureas were applied to cotton and cotton-polyester blends from azeotropes of water and an organic solvent. In some instances, the N-methylolated ureas were applied in emulsions of perchloroethylene, water, and an organic acid catalyst.

Two commercially available diepoxides, Araldite RD–2 and Eponite 100, were reacted with cotton-polyester sheeting. Solvents used were methanol, water, dioxane, *t*-butanol, and azeotropic mixtures of water and *i*-propanol and of water and ethanol. With Araldite RD–2 or Eponite 100 and a 50–50 blend, wrinkle recoveries of 300° wet and 280° dry (W+F) were obtained when the epoxide and the $Zn(BF_4)_2$ catalyst were applied from methanol, and the fabric retained 80% of its original breaking strength and possessed a resistance to abrasion that exceeded that of 100% cotton fabric of similar construction. The blend consisting of 80% cotton threads in both warp and fill directions, when treated with Eponite 100 under mild conditions, exhibited a 70° (W+F) increase over control values in wet and dry recoveries while maintaining 90% of its original breaking strength. The DP rating of these fabrics after five home launderings was 4.5.

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[2] Berni, R. J., Soignet, D. M., and Benerito, R. R. 1970. Anion-exchange cottons prepared from sodium cellulosate. Text. Res. J. 40: 999–1006.

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Dimethyloldihydroxyethyleneurea with a $Zn(NO_3)_2$ catalyst, when applied from an azeotropic mixture of water and *n*-propanol or water and ethanol to 50–50 blends and cured at low temperature, produced fabrics with recoveries of 300° (W+F), and excellent tensile properties. A blend of 80% cotton treated similarly increased 60° (W+F) in both wet and dry recoveries.

Stable emulsions of various *N*-methylolureas, water, perchloroethylene, and monochloroacetic acid were prepared. Cotton fabrics were padded with these emulsions and cured. Add-ons were comparable to those achieved with all-aqueous solutions. Wrinkle recoveries, however, were somewhat less for the fabrics treated with the emulsions.

Cottons containing anionic or cationic sites can be reacted at relatively low temperatures in nonaqueous media with a variety of cotton finishing reagents to produce DP cottons with selected properties especially suited for use in cotton-synthetic fiber blends. Conventionally used dimethylolated ureas can also be used in selected organic solvents or in binary solvent systems containing relatively small amounts of water to finish all-cotton fabrics as well as blends. It is very probable that completely nonaqueous processes or processes based on use of organic solvents in combination with smaller amounts of water can be developed. Closed systems based on recycling of solvents might be of interest to the textile industry if it is faced with problems of minimizing air and stream pollutions.

NEW MINERAL DYES FOR COTTON FABRICS

By C. James Conner[1]

Although organic dyes exceed mineral dyes in variety and brightness of colors, mineral dyes are preferred for cotton fabrics where light screening, color retention, and durability to leaching and outdoor weathering are required. Mineral colors have been limited to Pearl Gray (hydrated chromium oxide) and a few other less important shades. Conventional application of mineral dyes requires two-bath, double-decomposition systems, followed by multistep procedures for applying fungicide and water-repellent finishes.

The object of this work has been to introduce several new types of mineral dyes for cotton fabrics with a variety of shades and good potential for industrial use. Many of these new shades are produced with single-bath systems, requiring only a pad-dry-cure procedure to deposit the pigment. In some instances, both dye pigment and fungicide can be deposited together from a single bath.

A significant improvement in bath formulation and application resulted with the development of "single bath" mineral dyeing, by which a variety of new shades and fungicidal dyeings are produced with minimal processing procedures. New mineral dyeings, such as Zirchrome (fungicidal gray green), Zirchrome Chloride (greenish gray), Bright Orange (iron oxide-zirconia), Turnbull's Blue (ferrous ferricyanide-zirconia), Cobalt Pink (cobalt oxide-zirconia), and Cobalt Lavender (fungicidal cobalt-copper-zirconia pigments) have been developed and applied through single-bath processing. All of these color shades are deposited by heat decomposition of aqueous-unique chemical bath systems, resulting in insoluble pigment color shades which are stable to hot water washings and light. The cobalt colors are less resistant than the others to outdoor weathering, but have excellent indoor stability. The cobalt-copper pigments are significantly active in resistance to micro-organisms.

The conventional Pearl Gray chrome mineral-dyeing process has been modified to produce two new shades, Greenish Gold and Olive Drab. This modification involves adding ferrous sulfate to the chromic chloride bath, and heating the alkali-precipitated pigmented fabric with the residual alkali on the fabric. Each of these colors demonstrates resistance to water washing and weathering, and the Olive Drab could prove of interest to the military.

All of these mineral dyeings can be wax-finished and wax-fungicide-finished for water repellency and protection of the dyed fabrics from micro-organisms.

Chemical cost data are based on the described bath formulations using reagent-grade chemicals in most instances. Although these figures would be considerably higher than those based on crude- and technical-grade materials, in most instances they are comparable to the chemical bath costs in conventional chrome mineral dyeing. The average bath costs are in the range of $0.06 to $0.13 per pound, with the exception of cobalt dye baths. The higher cost of cobalt compounds, particularly reagent grade, results in bath costs of $0.20 to $0.21 per pound.

Aside from the introduction of a variety of new mineral colors, the work demonstrates the feasibility of single-bath mineral dyeing and the possibility of three-color shades by modifying conventional Pearl Gray processing.

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SOME MOISTURE PROPERTIES OF HIGH-PERCENTAGE COTTON BLENDS

By R. J. Harper, Jr., J. S. Bruno, E. J. Blanchard, and G. A. Gautreaux[1]

(Presented by R. J. Harper, Jr.)

Strength properties of polyester-cotton blends generally show substantial and progressive increases as the amount of polyester in the blend increases. This study was made to ascertain to what extent other fabric properties are affected by the polyester-cotton proportions in the blends. Two series of fabrics varying from all-cotton fabric to a high-polyester blend were obtained. One series consisted of sheeting with polyester contents of 10%, 20%, 34%, and 50%. The second series consisted of broadcloth with polyester contents of 10%, 20%, 34%, 50%, and 68%.

The comfort properties investigated were primarily moisture properties. The specific tests employed measured rate of absorption, rate of wicking, total moisture transport using a fabric wick and a sponge wick, total absorption, water vapor transport, and moisture regain. In addition, some measurements were made on fabric wetness and thermal characteristics. These moisture properties are extremely dependent on fabric history. To obtain data characteristic of the various fiber compositions, thorough preparation procedures and exclusion of wetting additives from the fabrics to be tested are necessary requirements. In addition to fiber composition, the influence of various chemical treatments on moisture properties was investigated.

The broadcloth fabrics were given a cross-linking treatment with 9% dimethylol dihydroxyethyleneurea, and the moisture properties of these fabrics were investigated. Nearly equivalent properties were exhibited by the all-cotton fabrics and the blended fabrics with up to and including a 50% polyester content. In the 68% polyester fabric, there was a definite decrease in moisture transport using a fabric wick, the rate of absorbency, and the wicking rate, which became more evident after cross-linking. Water vapor transmission was unaltered at a given blend level whether or not the fabric was cross-linked. Two properties that showed definite sensitivity to blend level were moisture regain and the total absorbency of the fabric. These properties progressively decreased as the amount of polyester in the blend increased. Furthermore, for a given blend level, the cross-linked fabric showed a lower moisture regain and lower total absorbency than its non-cross-linked counterpart.

The polyethylene softener in the usual chemical finish was found to have a marked influence on many moisture properties. Cross-linked fabrics with a 0.5% to 1.0% polyethylene add-on failed to wick a distance of 2 mm or absorb one drop of water after 20 min. Total absorbency was low and erratic, and moisture transport was less than 10% of that of the same fabric either cross-linked or untreated. However, moisture regain values were as great as with cross-linked analogs, and water vapor transport was unaffected. The effect on moisture properties of several representative commercial softeners, including polyethylene softeners, polypropylene, silicones, and polyethylenes, was measured.

In addition to softeners, other polymer additives may have a similar influence on fabric moisture properties. The types of polymers investigated included polyacrylates, polyurethanes, nitrile copolymers, and vinyl copolymers. Good moisture properties in polymer-treated fabrics were attributed to hydrophilic groups on the polymer or to the presence of large quantities of emulsifying or wetting agents in the compound polymer mixture. Subsequently, it was found that various reactive additives which are also wetting agents can be included in the finish along with polymers or softeners to produce durable-press fabrics, whose moisture properties are similar to those of the same fabric cross-linked without any additive. Concentration studies were made to determine the level of reactive additive (generally 1%–2%) necessary to restore wicking, absorbency, and moisture transport properties to the various blended fabrics.

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In addition to the above, the influence of other chemicals, catalysts, and reactive additives on moisture properties was investigated. A similar examination was also made on the effect of different finishing systems useful in producing durable-press fabrics. Many of these systems use a softener in the finish, and the presence of this material tends to overshadow the effect of the finishing system.

Because mercerization is an effective medium for modifying the structure of cellulose, some of the fabrics in this study were mercerized and then cross-linked. In a series of fabrics with different fiber contents, the blend level had to be greater than 50% polyester before any appreciable decrease was noted in such moisture properties as the drop absorption rate, the wicking rate, and total moisture transport. The wicking rate, drop absorption rate, and moisture transport were comparable in cross-linked mercerized fabrics and cross-linked unmercerized counterparts. Moisture regains of the cross-linked mercerized fabrics, however, were significantly greater than their unmercerized counterparts although in each series the value decreased with increasing polyester content. Surprisingly, mercerization does not seem to improve total moisture absorption of the fabric relative to its unmercerized counterpart.

Other properties of the fabrics were investigated. In general, warmth qualities of matched-blend fabrics were relatively close in performance. Tests for fabric wetness indicated that the blended fabrics felt wet with about half the moisture content needed to make all-cotton fabrics feel wet. Similarly, there was some indication that temperature drop during equilibrium moisture transport was greater with the blended fabrics than with all-cotton fabrics.

Unfortunately, it is difficult to relate the above-mentioned properties directly to the comfort qualities normally associated with all-cotton fabrics or high-level cotton blends. The two properties that do show a positive effect throughout the different blend levels are total moisture absorption and moisture regain. An attempt was made to relate this latter property to body comfort connected with moisture transport in clothing. However, because even the high-level polyester blends still have a substantial amount of cotton in them, test data on moisture properties will reflect the blended composition rather than a clear-cut differentiation between fibers.

FLAME-RETARDANT COTTON AND SYNTHETIC FABRIC BLENDS

By Hubert H. St. Mard, Carl Hamalainen, and A. S. Cooper, Jr.[1]

(Presented by Hubert H. St. Mard)

Cotton fabrics rendered flame retardant by phosphorus compounds are suitable for wearing apparel and most indoor uses, but are unsuited for most outdoor uses unless protected from actinic degradation by coatings, sunlight screening pigments, etc. The most effective application for outdoor fabrics are multipurpose treatments based on chlorinated hydrocarbons and antimony oxide which require a high add-on from 35% to 70% and which cause fabrics to be relatively impermeable to air and water vapor. This paper reports preliminary results of studies on fibrous fire-retardant polymeric materials which, when blended with cotton, contribute to the textile properties of the predominantly cotton fabric instead of detracting from it, as happens if applied from a solution or emulsion.

One method of obtaining fire retardancy is to apply a phosphorus treatment to cotton-synthetic fabrics. To determine the efficiency of the treatment, experiments were run on mixtures of fibers treated with tetrakis (hydroxymethyl) phosphonium chloride (THPC) and inherently flame-retardant synthetic fibers. These experiments were performed on intimate blends in small pad form made by suspending small amounts of ground-up fiber (2 g) in 1% carboxymethyl cellulose, and filtering through a Buchner funnel.

An oxygen index (OI) technique was used to determine the burning characteristics of these pads after drying and equilibrating them to room conditions. An OI value of 0.260 or above is considered to be self-extinguishing (flame retardant).

One synthetic fiber was composed of polyvinyl alcohol and polyvinyl chloride and another of a copolymer of acrylonitrile and vinylidene chloride (modacrylic). Both are reputed to have excellent sunlight and microbial resistance. When mixed with flame-retardant cotton, these fibers did not cause an increase in OI values; in fact, significant reductions in OI values were noted. For example, a sample of 100% cotton treated with THPC-amide had an OI value of 0.357 and a sample of 100% polyvinyl alcohol and polyvinyl chloride had an OI value of 0.354, whereas a 50:50 mixture of these had an OI value of 0.294.

Acrylonitrile vinylidene chloride (modacrylic) fiber was mixed in pad form with cotton treated with tetrakis (hydroxymethyl) phosphonium hydroxide-ammonia vapor cure (THPOH-NH_3) to various levels. All OI values were high for the 100% as well as for high- and low-level blends. Adding antimony oxide to these blends caused no significant increase in OI. Also, antimony oxide caused no increase of OI in the 100% THPOH-NH_3 sample.

Samples composed of untreated cotton and modacrylic fibers (with and without antimony oxide) were evaluated. All levels of this mixture had relatively high OI values which were enhanced when antimony oxide was used.

Several knit or woven fabrics, scoured and unscoured, containing either 15% or 30% modacrylic were studied. With no chemical treatment, each fabric had a small increase in OI compared to untreated 100% cotton.

These fabrics were given a previously developed weather-resistant treatment with methylol melamine resin catalyzed with zirconium acetate. Unexpectedly high OI values—in the range of 0.238 to 0.273—were obtained by the application of this fabric finish by itself.

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An OI value of 0.360 was obtained for scoured knitted 70:30/cotton:modacrylic blend treated with methylol melamine containing antimony oxide. A loosely woven, scoured fabric (83:17/cotton: modacrylic) similarly treated had a value of 0.345. Use of a vinylchloride-vinylidene chloride copolymer and a high level of methylol melamine containing antimony oxide caused an increase in OI to 0.383 for the woven fabric. If OI values this high are necessary, they probably could be obtained by increasing the amount of modacrylic in the fabric.

Woven fabrics of three different weights of 4.5, 6.8, and 8.5 oz/yd^2 and containing 15% modacrylic in the fill only were prepared. These fabrics were of relatively tight weave. Medium-weight, scoured fabric (6.8 oz/yd^2) had the highest OI value (0.313 to 0.316) when treated with 10% and 17% melamine resin, respectively. This 6.8-oz untreated fabric seemed to be the most amenable for further treatment with cross-linking resins, such as used for durable press, as well as with resins intermediate between a cross-linker and polymer former. Also to be used were combinations of cross-linker and polymer former used in the Polyset process. Cross-linking resins were catalyzed with a mixture of zinc acetate and zinc nitrate. Fabrics treated with methylol melamine as a control had OI values very close to the previous treatments, demonstrating the reproducibility of the procedure. Of the cross-linking treatments, the best results were produced by modified glyoxal-based resin containing antimony oxide (OI=0.269). This value, which is not extremely high, could probably be increased by treatment with a higher concentration of resin, by an increase of antimony oxide, or by a combination of both.

On the basis of OI, mixtures of phosphorus flame-retardant cotton and inherently flame-retardant synthetics used in these experiments were not additive. Supplementary flame-retardant agents (including antimony oxide) did not significantly increase OI. However, supplementary flame-retardant treatments on cotton and flame-retardant synthetic blends were effective in increasing OI. These data indicate that flame-retardant fibrous polymers containing antimony oxide may be blended with cotton at levels as low as 15% to produce predominantly cotton fabrics with high OI values by application of either an effective outdoor nitrogenous or of a conventional durable-press finish.

EFFECTS OF MILK ON FIRE-RETARDANT COTTON FABRIC

By Austin L. Bullock[1] and Mary E. Carter[2]

(Presented by Mary E. Carter)

INTRODUCTION

Fires associated with flammable fabrics have been reported to cause 200,000 to 300,000 injuries each year; 2,000 deaths occurred in 1970 as a result of such fires.[3] The recent increasing concern for safety from the hazards of fire, especially for small children, has resulted in the establishment of Federal standards for the flammability of children's sleepwear.[4]

Cotton flannelette, whose flammable characteristics are well known, has for many years been the primary fabric used in children's sleepwear. In order to meet the Federal safety requirements, cotton fabrics must be treated with a durable flame retardant. The most satisfactory durable retardants are based on organic phosphorus and nitrogen compounds. These flame retardant materials can react with cotton cellulose or with each other to form polymers within the cellulose structure.

Studies have been made on the durability of flame retardancy with repeated laundering[5] of fabrics and on the effect of hardness of water used in laundering.[6] Little has been reported on the interactions among the flame-retardant finish, the cotton fabric, and common household soils. This paper reports on some of the effects on selected flame-retardant cotton flannelette fabrics of repeated soiling with milk and its subsequent removal in laundering. Properties studied were the durability of flame-resistant finish, strength retention, and resistance to abrasion.

MATERIALS AND METHODS

The fabrics used in this study were all 100% cotton flannelette. They are identified with their flame retardant treatment as follows:

TC-1	Untreated
TC-2	Pyrovatex
TC-5	THPOH/NH_3
TC-6	Modified Pyrovatex I
TC-7	Modified Pyrovatex II
TC-8	Modified Pyrovatex III
TC-9	THPOH/Urea
TC-10	THPOH/NH_3
TC-11	THPOH/NH_3

Only samples TC-1 and TC-2 were available commercially when the study began; since then, TC-11 has become available. All other samples were experimental.

Flame resistance was determined as described in the Federal standards for the flammability of children's sleepwear, DOC FF 3-71. Nitrogen was analyzed by a Micro-Kjeldhal method, resistance to tearing by ASTM method D1424-63, breaking strength by ASTM method D1682-64, and flex and flat abrasion resistance by ASTM method D1175-64.

All fabrics were given a preliminary process wash and tumble dry as described in AATCC method 124-1969, III B. Samples of each fabric were then soiled with milk by padding, squeezed to a wet pickup of 100% to 125%, and line-dried overnight. The dry, soiled samples were then laundered and tumble-dried by the AATCC procedure III B cited above. This soil-dry-launder-dry cycle was repeated a total of 50 times, with specimens removed for analysis at intervals of 0, 1, 5, 10, 15, 20, 30, 40, and 50 cycles. Unsoiled fabric samples were also laundered, dried, and sampled at these intervals.

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RESULTS

Four of the flame-resistant fabrics retained satisfactory flame resistance after 50 standard laundry cycles. One of the fabrics (TC-11) had been treated with THPOH/NH_3, one (TC-2) with Pyrovatex, and the others (TC-6 and TC-8) with unknown modifications of Pyrovatex.

Fabrics treated with Pyrovatex (TC-2) or modified Pyrovatex (TC-6 and TC-8) retained satisfactory flame resistance after 50 cycles of the soil-wash-dry procedure after being soiled with milk. Under the same conditions, the sample treated with THPOH/NH_3 (TC-11) failed the flame test at 40 cycles. With the exception of fabric TC-9, soiled samples failed the flame test after fewer cycles then did corresponding unsoiled samples. Since the flame resistance of fabric TC-9 was unsatisfactory originally, the soiled sample could not be expected to pass the flame test.

For most of the fabrics, loss of nitrogen was not significant. A statistically significant loss, although slight, was observed for fabrics TC-5, 6, 8, and 10. A slightly greater loss was usually observed for soiled samples than for corresponding unsoiled samples.

The effect of soiling with milk is more noticeable in the textile properties of the fabrics. Statistically significant effects of both soiling and repeated laundering were observed on the breaking strength, tearing strength, and abrasion resistance of most of the fabrics studied.

The improvement noted for both abrasion resistance and tearing strength of soiled samples over corresponding unsoiled samples was investigated briefly. Several of the laundered fabric samples were extracted with cyclohexane in a Soxhlet extractor. After removal of the solvent, a greaselike material was recovered. Chromatography of this material on a thin layer of silica gel indicated that three to five components were present. These materials appear to be either glycerides or fatty acids. Such materials often exhibit a softening or lubricating effect on textile materials.

CONCLUSION

The flame resistance of cotton flannelette treated with fire retardants is adversely affected by soiling with milk only when the treatment of the original fabric conferred only borderline resistance. In general, if the unsoiled fabric passes the requirements of DOC FF 3-71, the soiled samples will also pass. In this study, fabrics treated with a Pyrovatex or a modified Pyrovatex fire retardant provided the most satisfactory flame resistance.

The textile properties of the fabrics in this study showed only slight, although statistically significant, changes with repeated soiling. The best balance of textile properties was observed in a fabric treated with THPOH/NH_3 (TC-11).

ACKNOWLEDGMENT

The authors acknowledge the assistance of Matthew Donoghue and Mary Paddon in testing the fabrics.

EFFECT OF CARDING VARIABLES AND COTTON-POLYESTER BLENDS ON CARDING EFFICIENCY AND PROCESSING PERFORMANCE

By Jack Simpson and Louis A. Fiori[1]

(Presented by Jack Simpson)

Cotton and synthetic fibers are usually blended at the drawing process; however, it is difficult to achieve fiber homogeneity with this technique which introduces problems in dyeing and in maintaining consistent product quality. Blending in the opening and picking room is increasing in an attempt to obtain a more intimate blend. Consequently, carding becomes a critical stage of operation, since the quality of yarn and resultant fabrics depends mostly on the card sliver quality. This paper discusses an investigation of machine variables that could result in higher carding efficiency and product quality, thus maintaining the inherent qualities of cotton during carding.

EXPERIMENTAL METHOD

A medium-staple cotton of average fiber properties and a high-modulus polyester of 1.5-inch staple length and 1.5 denier were blended in the opening and picking processes into blend levels of 100C, 80C/20P, 65C/35P, 50C/50P, 35C/65P, and 100P. These blends were processed into 36/1 yarn, using lightweight and heavyweight card slivers carded at a constant production rate of 30 lb/h by varying the doffer speeds. Carding efficiency was judged by card waste determinations with the Shirley analyzer, cylinder loading, sliver uniformity, and fiber orientation; yarn quality by yarn properties; and spinning efficiency by end breakage.

RESULTS

Card Loading

Increases in polyester content in the blend caused increases in bulk compression recovery (resiliency) and shear friction. The increase in friction offset the increase in compression recovery, so that cylinder load increased as the percentage of polyester in the blend increased. This caused fiber hooks and short-term card-sliver variability to increase. The increased fiber friction and length of the polyester fibers improved drafting so that fiber orientation and uniformity of second-drawing sliver, roving, and yarn improved with the increases in polyester content. The results demonstrate that the fiber characteristics needed for efficient carding (coarse fiber with low friction and good compression recovery) are opposite to those required for good drafting and yarn strength and uniformity (fine fibers with high friction).

Card Waste

Very little polyester was lost in the card waste, even though card settings normally employed for 100% cotton were used. With these settings, the cotton was carded more efficiently than with card settings commonly recommended for cotton/polyester blends.

Whereas the cylinder load increased with increased polyester content, the load per flat decreased, indicating that the fiber properties which increase cylinder loading are not necessarily those that increase flat loading. Previous studies on cotton had shown that as the flat speed decreased, the cleaning efficiency improved; that is, there were more motes and trash in the flat strips and less spinnable lint. The polyester having no neps, trash, or short fibers was not retained by the flats, especially at low flat speeds. However, its high frictional properties increased cylinder loading, which limits card production rates.

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Yarn Properties

No substantial changes in yarn grade occurred as polyester content in the blends increased, even though the grade for 100% cotton yarn was B and for polyester yarn A. For blends of carded yarns, the cotton grade apparently is the dominating factor and increasing the polyester content did not improve yarn grade. The twist multiplier for maximum strength decreased, and yarn strength and elongation increased as the polyester content increased. The increase in yarn strength and elongation with the increase in polyester content followed close to Hamburger's prediction[2] based on the strength-elongation curves of the cotton and polyester fibers.

End Breakage

Spinning end breakage for the blends was more critically affected by changes in tensor settings (apron openings) than by changes in break drafts. At constant end-breakage rate, twist can be reduced and front roll revolutions per minute (production rate) can be increased with increases in polyester content. Limited experiments indicate that the spinning drafting force, end breakage curves recently developed by Graham and Bragg[3] can be used to explain the interrelationships of blend, fiber orientation, and tensor settings. At low drafting forces, end breakage is usually high due to lack of fiber control (wide tensor settings) in the drafting zone. As fiber control is increased (narrowing of the tensor settings), drafting force increases and end breakage decreases until a minimum point is reached. Further increases in drafting force (further narrowing of the tensor setting) overcontrols the fiber and actually increases end breakage. In spinning the blends, a tensor setting that overcontrolled the fiber in the drafting zone was used. However, by increasing tensor setting, end breakage usually decreased. This demonstrates that to obtain the lowest end breakage for blends and to realize the fullest potential of the cotton component, it is important that the spinning variables selected (especially the tensor settings) do not overcontrol the fiber in the drafting zone.

ACKNOWLEDGMENT

Measurements of roving drafting tenacity were provided through the courtesy of J. Graham, Market Quality Research Station, Agricultural Research Service, U.S. Department of Agriculture.

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EFFECT OF DRAWING AND ROVING PROCESSING VARIABLES AND COTTON/POLYESTER BLENDS ON ROVING QUALITY

By Gain L. Louis and Louis A. Fiori[1]

(Presented by Gain L. Louis)

The consumer trend is towards apparel of functional textiles, particularly durable press. Because all-cotton fabrics have had problems of strength and durability, blends of cotton and manmade fibers have penetrated traditional cotton markets, e.g., printcloth, broadcloth, sheeting, and denim.

Most of the textile industry combines the manmade and cotton slivers (combed or carded) at the drawing operation. To obtain good fiber homogeneity and high-quality slivers, rovings, and yarns, and to optimize each fiber's contribution, it is imperative that the processing variables be properly combined during these stages. Hence, a study was initiated to evaluate the processing variables at drawing, roving, and spinning. This report describes findings obtained at the roving stage.

EXPERIMENTAL METHOD

A medium-staple cotton (C) of average fiber properties and a high-tenacity polyester fiber (P) of 1.5-inch staple length and 1.5 denier were combined at the drawing process to produce blends of 80C/20P, 60C/40P, 50C/50P, and 30C/70P. These blends were processed into rovings with the following drawing and roving processing variables.

Drawing Frame

A Saco-Lowell 4/5 Versa-matic drawing frame was used with a No. 30 button spacing and 10 doublings and draft. The four combinations of drawing frame variables were (1) close setting with two processes, (2) close setting with three processes, (3) open setting with two processes, and (4) open setting with three processes.

Roll Settings

Position	*Closed (inches)*	*Open (inches)*
Front to 3d roll	2 9/16	2 5/8
3d to 4th roll	1 1/2	1 19/32
4th to back roll	1 13/16	2 1/16

All slivers were processed into 55 gr/yd with a front roll speed of 800 ft/min.

Roving Frame

Each drawing frame sliver was processed through the Saco-Lowell Rovematic roving frame with the following 27 combinations of roll settings and back drafts:

Blend	*Front-to-middle roll setting (inches)*	*Middle-to-back roll setting (inches)*	*Back draft*
80C/20P, 60C/40P, and 50C/50P	2	1⅝	1.6
	2⅛	1⅞	2.0
	2¼	2⅛	2.3
30C/70P	2⅛	1⅝	1.6
	2¼	1⅞	2.0
	2⅜	2⅛	2.3

Slivers of all the blends were made into a 1.0 hand roving. Roving quality was judged in terms of the coefficients of variation, visual slubbiness in combination with those detected on the Uster diagram, and draft wave characteristics interpreted from the Spectrograph diagram. The roving with the lowest coefficient of variation and free from drafting waves and slubs was considered to be best in quality.

RESULTS

The closed roll settings resulted in slivers of better overall quality than the open roll settings, regardless of blend level or stage in drawing (first, second, or finisher drawing). With all blends, three drawing operations produced slivers of better quality than two drawing operations.

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Increasing the roving frame middle-to-back roll settings from 1⅝ inches to 1⅞ to 2⅛ inches and increasing back draft from 1.6 to 2.0 to 2.3 caused consistent and highly significant degradation in roving quality, regardless of blend. Also, as middle-to-back roll setting was increased from 1⅝ to 2⅛ inches, roving quality reduction tended to be small at 1.6 back draft, large at the 2.0 level, and larger at 2.3. The relationship was direct, linear, and consistent, independent of the drawing process variables used.

A front-to-middle roll setting of 2⅛ inches yielded the most uniform roving for the 80C/20P, 60C/40P, and 50C/50P blends, and the 2¼-inch setting for the 30C/70P, for any given combination of back roll setting and back draft. Excessive roving end breakage occurred when the smallest front roll setting (2 inches) was used; slubs (sections of undrafted slivers) caused the breaks.

The nonuniformity of roving coefficients of variation was directly and linearly related to the percentage of cotton in the blend. The nonuniformity of the sliver was transformed into the roving but was magnified in rovings produced from blends containing more cotton. However, by properly selecting roving frame variables, it was possible to keep the rate of increase in nonuniformity from sliver to roving of the high-cotton-content rovings similar to that of the low-cotton-content roving.

Rovings of the best quality of the four blends were differentially dyed to examine their blending homogeneity. No appreciable visual differences were noted.

The combination of roving frame variables which produced the best roving quality with closed drawing frame roll settings and three drawing processes was as follows:

Front-to-middle roll setting:	2⅛ inches (for 80C/20P, 60C/40P, and 50C/50P). 2¼ inches (for 30C/70P).
Middle-to-back roll setting:	1⅝ inches (for all blends).
Back draft:	1.6 (for all blends).

INDIVIDUALIZING COTTON FIBER BY "SPIRAL" CARDING

By Roger S. Brown and Philip L. Rhodes[1]

(Presented by Roger S. Brown)

Textile machinery research at the Southern Regional Research Center is directed toward developing a fundamentally new cotton-processing system. One of the most difficult problems of the system is that of completely individualizing cotton fibers without fiber damage and placing them in usable condition for subsequent manipulation and yarn formation. Since present methods sacrifice fiber individualization in order to reduce fiber damage to an acceptable level, a new method of fiber separation was sought.

After extensive evaluation of many devices using aerodynamic, electrostatic, and mechanical forces to individualize fibers, it was determined that toothed rolls are still the most efficient means. Therefore, a study was conducted to determine the effects of roll diameter, surface velocity, centrifugal force, tooth density, and tooth angle on product quality. The study indicated that small-diameter rolls having a high tooth density and rotating at high speed are the most effective for individualizing or carding the fibers.

It is well known that loading the card cylinder has a detrimental effect on carding quality. It was found that cylinder loading can be eliminated if the cylinder is operated at a speed which will impart a centrifugal force of about 600 *g* to the cotton fibers. At this speed, the fibers will escape from the teeth by centrifugal force. The smaller the diameter of the cylinder, the smaller the fiber velocity required for the cylinder to be self-stripping, thus reducing the chance of fiber damage. There are two advantages of operating a cylinder at self-stripping speed: (1) cylinder loading is eliminated, allowing the teeth to card at maximum efficiency, and (2) the fibers are projected by centrifugal force against any cooperating carding surface.

It was determined that a self-stripping cylinder with a small diameter (3 to 4 inches) was the best approach for individualizing cotton fiber. Tests proved that worker rolls operated in conjunction with the self-stripping cylinder receiving fibers from a conventional licker-in were superior to a conventional licker-in feed-plate arrangement because the fibers were not positively held. This minimized fiber damage, but space limitations around the small cylinder restricted the number of worker rolls which could be used.

A new technique utilizing the advantages of a high-speed small cylinder was devised. It eliminated the use of licker-in feed plates, multiple worker rolls, and extensive carding surface area. It requires feeding and forcing tufts to spirally traverse the length of a small carding cylinder which is surrounded by a concentric granular carding surface and a longitudinal contoured channel or duct. The carding cylinder is 4 inches in diameter and 12 inches long; it rotates at a self-stripping speed of 5,000 r/min. Suction is applied to one end of the channel, and tufts are fed to the opposite end. Upon entering the channel, the tufts are engaged by the cylinder teeth and carried around the cylinder past the carding surface. Upon reentering the channel, the cotton is thrown clear of the teeth, and the airflow created by the suction advances the fibers toward the discharge end. The forward momentum of the tufts and the cross-sectional shape of the channel cause the fibers to become reengaged by the teeth of the cylinder. The combined action of the suction and the revolving cylinder causes the tufts to follow a spiral path. The number of carding cycles is determined by the amount of suction, channel shape, length of the toothed cylinder, cylinder speed, and tuft size. Individual fibers, because of their low mass, tend to pass directly through the airflow channel, thus assuring that the fibers will not be overworked.

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Several grit sizes for the granular material have been evaluated in conjunction with a wide range of toothed wire on the cylinder. A fine grit provided the required carding surface for complete fiber separation with no loading, whereas a low tooth density provided space for the tufts during the initial carding cycles. The tufts were completely separated into individual fibers; however, some fiber breakage did occur at practical production rates. Using a rotating wire-clothed worker roll in conjunction with the card cylinder practically eliminated fiber damage.

A variation of the spiral carding principle, designed to provide a means of feeding individual fibers into open-end spinning systems, is shown in figure 1. It consists of two cylinders, 3¼ inches in diameter and 2 inches long. The first cylinder performs the functions of both feed roll and worker roll. It is clothed with metallic card-doffer wire and rotates with the teeth pointing in the negative direction. A narrow feed plate is located at one end of the cylinder for feeding a ½-inch-wide supply of cotton. The second cylinder is clothed with metallic card-cylinder wire and rotates in the positive direction at 5,000 r/min.

To eliminate the need for suction and to provide positive control of the number of carding cycles, the top half of the card cylinder cover has four spiral grooves. With the card cylinder rotating at self-stripping speed, the fibers are forced by the grooves to spiral the cylinder four times in traversing the two-inch-wide cylinder. The bottom half of the card cylinder cover may be utilized for cleaning by providing slots, a screen section, or grid bars.

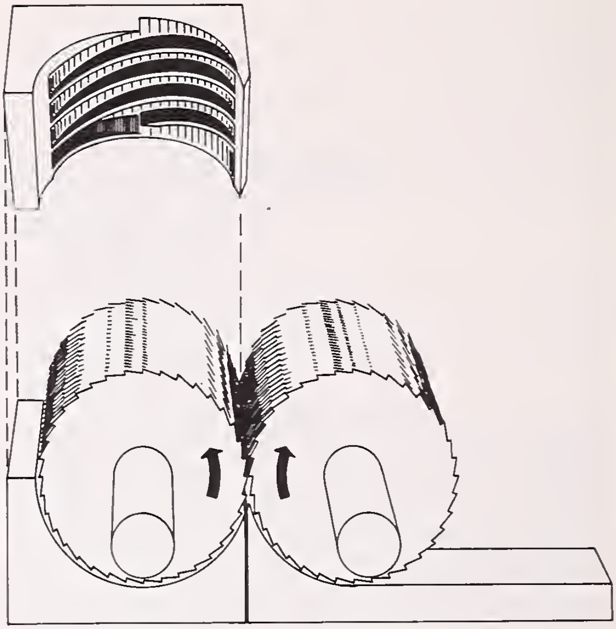

FIGURE 1.—Detail of self-spiraling cards.

The carding takes place between the two cylinders, with the four spirals giving the equivalent of four worker rolls. An opening is provided in the top housing at the end of the cylinder where the fibers are discharged by centrifugal force and are carried away by a low-volume airstream created by the cylinder.

This arrangement produced complete fiber separation with no fiber breakage at production rates sufficient for either conventional or break spinning. It is anticipated that this unit will be incorporated into the new cotton-processing system for individualizing fibers. This principle of carding has the potential to meet present-day card production rates; however, additional research is necessary to scale up the spiral card for high production.

IMPROVING THERMAL AND ELECTRICAL CONDUCTIVITY OF COTTON FABRICS BY CHEMICAL PLATING

By Devron Thibodeaux and Albert Baril, Jr.[1]

(Presented by Devron Thibodeaux)

Untreated cotton fibers and fabrics are characterized as both electrical and thermal insulators. Significant changes in these characteristics could suggest a number of new uses for cotton. For example, the establishment of electrical conductivity in cotton would provide a method of reducing the nuisances and hazards associated with the static electrification of textiles. Also, increasing cotton's thermal conductivity should increase its use where the ability to transfer or dissipate heat is desirable.

Recent studies carried out at the Southern Regional Research Center have provided a means of increasing both the electrical and thermal conductivity of cotton textiles by chemically plating their surfaces with a continuous metallic coating. Until now, the well-known process of chemical or electroless metal plating[2] has been limited to the coating of surfaces of either conductive metals or catalyzed plastics. The significant accomplishment of this research has been the application of electroless metal plating to the coating of cellulosic materials.

In order to chemically plate the surfaces of nonconductive fibers, such as cotton, it is necessary to make the surfaces catalytic. One way of accomplishing this is to first sensitize the fibrous material in an aqueous solution of stannous chloride, then treat it with an activating solution of palladium chloride. This procedure allows the elemental palladium catalyst to be deposited onto and into the fibrous surfaces by the spontaneous oxidation of the absorbed stannous ions to stannic ions and the concurrent reduction of palladium on the fibrous surfaces forming activated sites. Certain metal ions can then be deposited at the activated sites by reduction taking place in the plating solution. In most cases the metal salts used are cobalt (II) or nickel (II) chloride, with sodium hypophosphite as the reducing agent. To maintain a continuous plating action and to prevent metal from precipitating in solution, certain carboxylic acid salts, such as rochelle salt or sodium citrate, are added to the plating solution. These agents form water-soluble complexes with the dissolved metallic ions and thereby maintain the metal in solution. Ammonium chloride is used in the plating solution to control the rate of metal deposition. This rate is also controlled by the pH and temperature of the plating bath.

The continuity and quality of the metal coatings were evaluated by scanning electron microscope (SEM) photographs of the coated fabric surfaces. An interesting feature of this work was that SEM photographs were obtained without the usual vacuum deposition of gold metal on the sample surface, proving that the chemically plated metal layer is continuous and thick enough to reproduce an excellent photograph without the buildup of electrostatic charge causing washout spots in uncoated areas. An obvious explanation of this phenomenon is that the metalized coating serves to conduct away excess charge.

A series of measurements was performed to determine the electrical properties of the metalized fabrics. Simple resistance measurements indicate that the coating is uniform and matches very closely an ideal type of conductor with an electrical resistance that varies linearly with the length of the conductor and inversely with its cross-sectional area. The data also show a direct relation between metal add-on and conductivity. A nominal value of the conductivity of the metalized cotton is 1.0 mho cm^{-1} as compared to the conductivity of pure cotton cellulose of the order of 10^{-10} mho cm^{-1}.

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[2] Brenner, A. 1954. Met. Finish. 52(11): 68–76; 52 (12): 61–68.

It was reasoned that the enhanced electrical conductivity of the metalized fabric would allow the static charge to migrate more rapidly and leak into the atmosphere. To investigate the point, a precision electrometer was used to measure the percentage of charge remaining on a control and on a metalized sample at varying times after they were electrically charged. As the time after charging increased, the charge remaining on the metalized sample was less than half of the charge still on the untreated control. Likewise, it was found that if an edge of the metalized fabric was touched to a ground point, the residual charge as measured by induced voltage was practically zero. This was not the case with the control sample.

The ability to impart a high degree of electrical conductivity to cotton textiles by electroless plating has far-reaching applications. This technique could eliminate the annoying and sometimes hazardous conditions associated with electrostatic charge in textile products. The use of cellulosic fibers, yarns, or fabrics made conductive by electroless plating and incorporated into carpet construction could dissipate the charge built up when a person strides over the carpet in a room where the humidity is low.[3] These products could be incorporated into the textiles used in hospitals and particularly in operating rooms,[4] where the danger from electrostatic discharge is increased by the dry, combustible atmospheres present.

The great enhancement in electrical conductivity of the metalized fabric suggested that the thermal conductivity of the metalized samples should have increased also. Since the direct measurement of the thermal conductivity of a cloth sample is difficult, the following experiment was designed to study the thermal diffusibility of the metalized fabric.

A block of Formica was fabricated and two small holes were drilled through it. A pair of matched Chromel-Alumel thermocouples were inserted into the holes so that the tip of each thermocouple was just at the level of the upper surface of the Formica block. A square of the metalized fabric (2.5 by 2.5 inches) was placed over one thermocouple, and a sample (same size) of untreated fabric was placed over the other thermocouple. A ⅜-inch heater tape was laid across the top of both fabrics and centered over the location of the two thermocouple holes. The entire top surface was then covered with sheet asbestos and weighted down with a 1-inch-thick insulating block. When heat was applied to both samples, the temperature below the surface of the control rose more rapidly than that of the metalized fabric.

The ability of the metalized fabrics to transport and dissipate thermal energy also can be useful. In trying to solve the problems of fabric flammability and flame retardance, very little attention has been given to conducting the heat away from the location of the ignition source on the fabric. The possible contribution of electrolessly metalized fibers, yarns, and fabrics to the flame retardance of garments, mattresses, upholstery, and drapery should be investigated. Besides the protection given by thermal conductivity, the metallic coating should also add a higher degree of reflectivity of thermal radiation which could increase protection to people involved in firefighting.

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[3] Lewis, H. F. 1972. Text. Inst. Ind. 10(7): 199–203.

[4] Guest, P. G., Sikora, V. W., and Lewis, B. 1953. U.S. Bur. Mines Bull. 520, pp. 7–21. Beach, R. 1964. Chem. Eng. 71(26): 73–78.

PROCESSING FACILITIES AND PROGRAM FOR RESEARCH ON COTTON KNITS

By E. C. Kingsbery and G. F. Ruppenicker, Jr.[1]

(Presented by E. C. Kingsbery)

The knitting industry has expanded rapidly in recent years. Since 1960, the use of knits in the United States apparel industry has increased from less than 25% to over 40% of the market. Most estimates show that within the next few years well over half of all the garments produced in this country will be knits. Cotton, however, has not shared in this growth. As recently as 1956, over 50% of all yarns consumed in knit apparel were cotton. This percentage has steadily declined, and in 1970 only about 37% of the knit apparel market was held by cotton.

Although cotton yarns have been successfully knitted for many years, their use has been generally limited to the coarser counts and heavier constructions. However, the greatest growth potential for knits is in the outerwear markets, such as slacks and suitings. Most of these outerwear fabrics are produced in complex, fine-gage knitting machines that require premium-quality yarns. Cotton yarns often lack the strength, smoothness, uniformity, and freedom from imperfections to make them suitable for many of these finer-gage, lighter-weight fabrics. Another problem is the tendency of cotton yarns to shed excess lint during the knitting process which causes fabric defects and problems in maintaining proper tensions.

To help strengthen cotton's competitive position in this market, a knitting research program was initiated at the Southern Regional Research Center. A knitting laboratory was planned and constructed, and equipped with the latest types of machinery for producing most types of knitted fabrics. Included were five production-size circular knitters, a V-bed knitter, tricot and Raschel warp knitters, a warper and 400-end creel, several laboratory-scale knitters, and other auxiliary equipment.

The knitting research program is currently directed toward developing higher quality cotton and cotton-synthetic blend knitting yarns that will be suitable for producing fine-gage fabrics. Studies are being conducted to determine the effect of cotton fiber properties on yarn quality and performance. Cottons grown in different areas may vary widely in strength, length, uniformity, and fineness depending upon the variety, growing season, weather conditions, and harvesting methods. The proper selection of cottons based on fiber properties can result in improved yarns for knitting.

A related area of research has as its objective to improve the knitability of cotton yarns through the use of improved processing techniques. Cotton yarns of superior evenness and tenacity, and of the quality normally required for double knits, have been produced from a selected blend of Upland and high-strength California cottons. In this study, the effects of various mechanical processing variables at carding, combing, and spinning were evaluated in order to determine the optimum processing procedures.

Similar studies are now underway with blends of cotton and polyester. Efforts are being made to establish the best blend levels and blending techniques for producing knitting yarns.

Another approach is concerned with minimizing the deficiencies of cotton knitting yarns through chemical treatments. This work is being done under contract at the Philadelphia College of Textiles and Science. Various coating materials have been applied to cotton yarns from both aqueous and solvent systems. Many of the treatments improved strength and smoothness, and reduced the linting tendency of the yarns.

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THE TAPER AND ITS RELATION TO THE PHYSICAL PROPERTIES OF COTTON FIBERS

By K. N. Seshan[1]

(Presented by Wilbur F. McSherry)

ABSTRACT

In this study, an attempt was made to define taper and to examine the relationship between fiber-end taper and the gross physical and fine structural properties of cotton. Detailed investigation has shown that taper varies in different cottons, and that it can be characterized for a cotton by making measurements on the model length group.

Tenacity of fiber bundles was highest at the middle and least at the tip portion. Also, taper was found to influence the surface properties of cotton fibers as revealed by the differential frictional effect of alined fiber fringes. Studies of fine structure revealed that the birefringence of the fiber increases significantly from root to tip through middle. The X-ray crystallite orientation at the root was also found to be significantly lower than the other region. These observations lead to the inference that the chain molecules become better alined as one proceeds from the root to the tip of a fiber. This change in orientation appears to be influenced by the fiber profile.

INTRODUCTION

From the few research studies reported in the literature on the differences in maturity,[2] frequency of reversals,[3] and diameter of the primary wall along the fiber,[4] it may be inferred that there is a variation in the gross and fine structures of the cotton cellulose within a fiber. However, there has been so far no systematic or extensive study on the variation in either the diameter of the fiber or the orientation of the cellulose crystallites in the technologically important fully grown cotton fibers. A study of the gradual variation in ribbon width (taper) assumes importance because the taper could be expected to affect the structural and physical properties of fibers, such as crystallite orientation, birefringence, uniformity of strength along the length of the fiber, and the processing characteristics, such as hook formation and migratory behavior of fibers in yarn. This paper attempts to define and quantitate taper, thus far understood only in qualitative terms, and examine its relation to the physical properties of cotton fibers.

METHODS AND MATERIALS

If a knowledge of fiber profile, either ribbon width or linear density along the length, is available (fig. 1) then the fiber-end taper may be statistically and geometrically defined in the following manner:

1. The coefficient of variation of ribbon width or linear density of the fiber at definite intervals along the length of the fiber.
2. The length of the fiber whose ribbon width or linear density is less than the average values (T-mean$=D'B$).

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[1] Senior scientific officer, the South India Textile Research Association, Coimbatore, India.

[2] Goldthwait, C. F., Smith, H. O., and Barnet, M. P. 1947. Text. World 97: 105.

[3] Wakeham, H., and Spicer, N. 1955. Text. Res. J. 25: 585.

[4] Pearson, N. L. 1950. Text. Res. J. 20: 152.

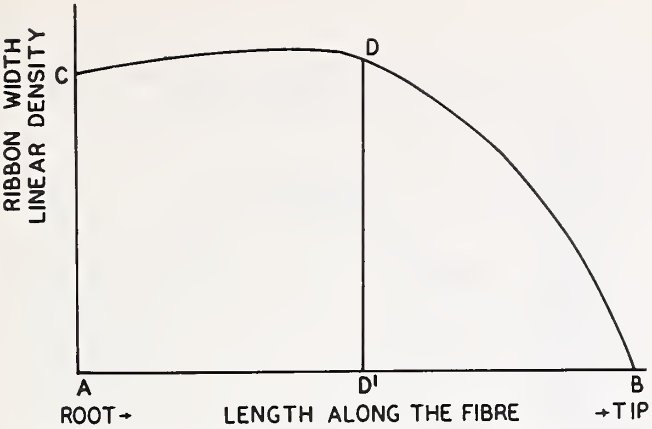

FIGURE 1.—Construction of different measures of taper from a hypothetical fiber profile. DD′ is the average ribbon width or linear density.

3. The ratio of the average ribbon width or linear density to the length of the fiber whose ribbon width or linear density is less than the average value of ($T\text{-slope}=\frac{DD'}{D'N}$).

In this paper, the taper parameter T-slope obtained from the profile based on the linear density measurements alone is considered.

Preliminary investigation on taper was carried out on 7 cottons; 24 cottons were studied for gross physical properties and 12 cottons for frictional, mechanical, and fine structural properties.

Preparation of Sliver

Since a similar root tip orientation of all fibers in a bundle was essential for these experiments, a special procedure was followed in the preparation of the hand sliver. Samples of cotton were procured in seed cotton form and ginned by hand so that the root ends of the fibers could be alined. The alined tufts were drafted and doubled without disturbing the direction of the root and tip ends to obtain the required sliver.

Measurement of Taper

Fibers belonging to each length group were alined so that the tip ends pointed in one direction. This taper-oriented bundle was transferred to a cutting device fabricated here and cut into 2-mm segments. After determining the weights of the consecutive segments of these fiber bundles from the root to tip region for each length group, a profile of the average fiber characteristic of the group was constructed by dividing the linear density of the fiber segment by the number of fibers in the bundle. From the profiles thus obtained, the taper parameter T-slope was calculated. Ten bundles were tested for each length group of cotton.

Fiber fineness, 2.5% span length, and fiber tenacity were determined with the Digital Fibrograph, Micronaire, and Stelometer, respectively.

Friction

Coefficient of friction values were determined on pairs of fringes with (1) root ends alined and gripped but tip ends free (μ_T), (2) tip ends alined and gripped but root ends free (μ_R), and (3) randomly oriented fiber ends (μ_g) under five levels of loads ranging from 30 to 300 g. Ten pairs of fringes were used for each test. An instrument[5] fabricated here was used for this purpose.

Mechanical Properties

Root-tip-alined fiber bundles belonging to the model group length of the cottons were taken and tested for mechanical properties at the root, middle, and tip regions on the Instron tensile tester with a cross head speed of 2 mm/min. Pressley clamps were used and the test length was 3 mm. Ten readings were taken for each test.

Birefringence and Optical Orientation Factor

The well-known Becke line method was used to determine the birefringence of the fibers. The variation along the length of the fiber was studied by scanning 4 parts in each of 3 regions of the fiber, the root, middle, and tip. The optical orientation factor (f_o) was computed by comparing the birefringence for a cotton to that of ramie (0.0619) as determined in the present work. The temperature was maintained throughout at 30°±0.5° C.

X-Ray Orientation Factor

Root-tip-alined fiber bundles belonging to the model group length of the cottons were dewaxed and mounted on a specially designed clamp, which could be conveniently moved in the texture goniometer, so that any desired part of the fiber along its length could be exposed to X-radiation (CuK_{α}). The fiber bundle was pre-tensioned and scanned point by point along the 002 arc, noting the counts per fixed time (64 s). Orientation factor was calculated by the well-known formula of Hermans:

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[5] Viswanathan, A. 1966. J. Text. Inst. 57: T30.

$$f_x = 1 - 3/2\ \overline{\sin^2 \alpha},$$

where

$$\overline{\sin^2 \alpha} = \frac{\int_0^{\pi/2} F(\alpha) \sin \alpha \cos \alpha\, d\alpha}{\int_0^{\pi/2} F(\alpha) \cos \alpha\, d\alpha},$$

where $f(\alpha)$ is the intensity distribution in the paratropic reflection. Two bundles were tested for each test.

RESULTS AND DISCUSSION

Determination of Taper

The general profile obtained for a cotton based on linear density measurements is shown in figure 2. The linear density increased from the root to a maximum somewhere in the middle of the fiber (40% to 60% of the length) and then decreased sharply. The root part also showed a tendency to taper but the extent of taper was small and inconsistent in most of the bundles and therefore could not be effectively quantified in terms of taper parameter.

The parameter T-slope was estimated from the profiles obtained for bundles. An analysis of the data revealed a wide variation in the values of taper and a significant association with fiber length within a cotton, the correlation coefficients varying from —0.49 to —0.95. Table 1 gives the data obtained for taper for different cottons.

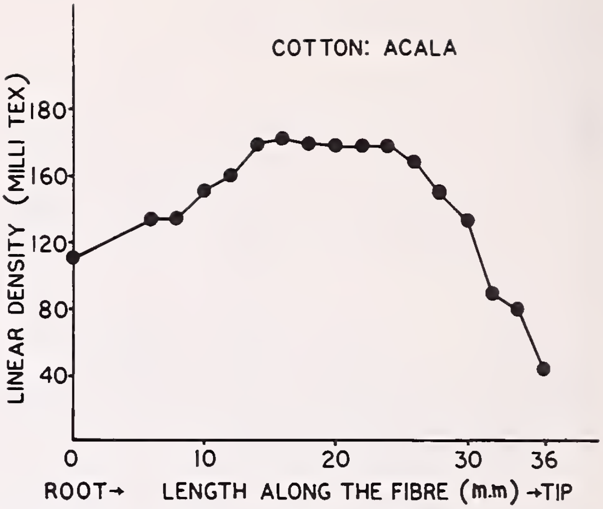

FIGURE 2.—Profile of a single fiber estimated from linear density measurements on a fiber bundle.

If, however, taper for a given cotton must be characterized by a single measure, it would be preferable to estimate it from fiber belonging to (1) a length group common to all cottons or (2) the model length group for each cotton. Of these, the second alternative would be more characteristic. A comparison of the taper values obtained for different cottons from model lengths (table 2) showed significant differences among cottons.

The taper values and physical properties of 24 cottons belonging to different botanical species are given in table 3.

TABLE 1.—*Taper values (fiber bundles) for different length groups within a cotton for different cottons*

[T-slope (millitex/mm)]

Length group (mm)	Cotton						
	'Digvijay'	'Sanjay'	'PRS-72'	'MCU-1'	'Acala'	'MCU-4'	'Gujarat-67'
23–24	25.5	41.6	58.6	61.6	....	....	....
25–26	24.1	31.7	39.8	41.3	....	....	....
27–28	17.3	25.6	38.1	31.4	....	....	....
29–30	21.2	24.1	24.0	25.7	33.6	....	....
31–32	15.5	19.7	22.9	25.0	34.3	30.3	35.6
33–34	11.8	14.0	22.3	18.1	28.0	17.2	22.3
35–36	....	14.8	16.4	15.4	19.2	16.5	16.0
37–38	....	....	....	19.0	14.9	14.3	17.5
39–40	....	....	....	....	12.8	10.4	13.1
41–42	....	....	....	....	15.5	10.3	10.6
43–44	....	....	....	....	....	8.5	8.3

TABLE 2.—*Taper values from fiber bundles belonging to the model length of different cottons*

Cotton	*T*-slope (millitex/mm)
'Acala'	18.4
'Digvijay'	22.5
'MCU 4'	10.8
'MCU 1'	23.6
'PRS-72'	30.9
'Gujarat-67'	12.3
'Sanjay'	26.0
C.D.	3.83
Sensitivity	5.3

Analysis of Taper in Species

It is generally observed that *Gossypium barbadense* tends to have a low taper value (table 4), i.e., these cottons have a smaller angular width at the tip than other varieties. However, these observations are based on few cottons only.

TABLE 4.—*Maximum, minimum, and range of taper values observed for cottons belonging to various species*

Species	No. of samples	*T*-slope (millitex/mm) Maximum	*T*-slope (millitex/mm) Minimum	Range
G. hirsutum	12	39.0	18.4	20.6
G. barbadense	3	19.6	15.3	4.3
G. herbaceum	4	35.7	20.7	15.0
G. arboreum	5	31.1	19.6	11.5

Taper and Fiber Properties

The correlation coefficients of taper with fiber properties are given in table 5.

It is interesting to note that among the fiber properties only fiber length is significantly correlated with taper. Thus taper could be considered essentially an independent property, possibly capable of explaining some of the processing characteristics of cotton.

TABLE 3.—*Taper values and fiber properties for different cottons*

Cotton	*T*-slope (millitex/mm)	2.5% span length (inches)	Tenacity (g/tex) 0 gage	Tenacity (g/tex) 1/8-inch gage	Drop in tenacity (%)	Fineness (micronaire)
G. arboreum:						
'A.K. 235'	24.0	0.94	41.2	18.5	55.0	4.53
'Sanjay'	22.2	.94	40.4	24.5	39.4	4.40
'C.J. 73'	25.8	.90	44.4	25.5	42.6	4.94
'G.6 Bhahimsa'	31.1	.89	41.4	21.4	48.3	4.80
'Koilpatti-7'	19.6	1.14	45.2	24.7	45.4	5.00
G. barbadense:						
'Giza-7A'	15.3	1.27	40.8	26.0	36.3	3.70
'Sea Island'	19.6	1.34	37.8	22.8	39.7	3.41
'Sujata'	16.1	1.29	48.9	29.5	39.7	3.62
G. hirsutum:						
'Lakshmi'	23.3	.92	36.8	16.6	54.8	3.34
'Coker'	24.9	1.10	36.9	20.8	43.6	3.25
'Humphy'	28.2	.97	34.2	18.1	47.1	4.17
'DPL-16'	26.6	1.14	33.8	21.8	35.5	3.50
'Stoneville-213'	27.6	1.09	32.2	18.5	42.5	4.01
'Stoneville-7A'	28.1	1.11	36.3	18.9	47.9	4.00
'A-51-9'	39.0	.92	39.1	19.8	49.4	3.90
'PRS-72'	30.9	1.02	33.8	19.1	43.4	4.46
'MCU 1'	23.6	1.08	34.4	18.8	45.3	4.20
'Acala'	18.4	1.20	37.4	21.2	43.3	3.75
'Deviraj 170/CO2'	34.6	1.01	32.3	19.7	39.0	3.60
'Gujarat-67'	20.3	1.23	34.3	19.4	43.4	3.10
G. herbaceum:						
'Jayadhar'	28.7	.82	37.8	17.2	54.5	5.30
'Digvijay'	35.7	.91	44.2	26.0	41.2	3.80
'V-797'	25.3	.90	35.9	20.2	43.7	4.50
'Suyhodur'	20.8	.86	40.5	16.4	59.5	5.02

TABLE 5.—*Correlation between taper and fiber properties*

Fiber property	Correlation coefficient
2.5% span length	−0.59
Tenacity at 0 gage (g/tex)	−.28
Tenacity at 1/8-inch gage (g/tex)	−.30
Drop in tenacity	.12
Fineness	.11

Differential Frictional Effects in Cottons

The coefficient of friction obtained for three states of fiber-end orientation under different levels of normal loads for different cottons are given in table 6.

Statistical analysis revealed that there was a significant difference in the coefficient of friction between cottons under all levels of loads tried. Also, the interaction between cotton and state of fiber-end orientation was also significant in all loads. It was also found that the differences between μ_R and μ_T were significant for loads less than 150 g; μ_R was highest, and generally μ_T lowest. This showed clearly that a directional effect is present on the frictional behavior of cottons as in the case of wool fiber. The differential friction defined as $\frac{\mu_R - \mu_T}{\mu_R^{R}} \times 100$ was examined for its dependence on the taper of the cotton fibers for the two loads, viz 30 and 72 g, at which the statistical analysis showed a significant difference between μ_R and μ_T. However, this

TABLE 6.—*Values of coefficient of friction*

Cotton	Particulars	Load 30 g	72 g	150 g	220 g	297 g
'A 51-9'	Tip-free	0.388	0.310	0.266	0.262	0.239
	Root-free	.379	.290	.251	.255	.223
	Random	.350	.272	.210	.235	.208
'Stoneville-213'	Tip-free	.396	.335	.270	.258	.224
	Root-free	.431	.368	.291	.274	.259
	Random	.359	.313	.266	.242	.212
'Digvijay'	Tip-free	.295	.275	.219	.221	.211
	Root-free	.313	.291	.198	.217	.200
	Random	.289	.263	.217	.229	.218
'Gaorani-6'	Tip-free	.315	.264	.221	.220	.207
	Root-free	.329	.266	.230	.230	.209
	Random	.315	.259	.233	.218	.195
'Acala'	Tip-free	.367	.300	.248	.237	.238
	Root-free	.377	.329	.289	.258	.248
	Random	.335	.303	.261	.242	.243
'Jayadhar'	Tip-free	.314	.245	.238	.216	.212
	Root-free	.368	.272	.233	.213	.205
	Random	.319	.241	.234	.225	.204
'Gujarat-67'	Tip-free	.400	.321	.257	.255	.242
	Root-free	.423	.347	.289	.268	.226
	Random	.367	.321	.269	.220	.222
'Sea Island'	Tip-free	.399	.314	.255	.249	.227
	Root-free	.411	.319	.261	.248	.229
	Random	.425	.326	.247	.254	.232
'Sanjay'	Tip-free	.322	.281	.252	.258	.226
	Root-free	.354	.298	.241	.241	.222
	Random	.351	.289	.245	.235	.227
'Sujata'	Tip-free	.323	.278	.243	.225	.215
	Root-free	.388	.326	.265	.244	.218
	Random	.360	.295	.254	.250	.218
'V-797'	Tip-free	.341	.289	.239	.256	.241
	Root-free	.395	.326	.256	.273	.241
	Random	.378	.309	.258	.263	.250
'Koilpatti-7'	Tip-free	.337	.299	.231	.237	.221
	Root-free	.341	.298	.242	.242	.225
	Random	.307	.276	.221	.238	.218

differential friction was found significantly correlated with the T-slope only at 70-g normal load, the correlation coefficient being —0.52. These observations indicate that when the fibers assume a more uniform cross section along the length, the differential friction would be a minimum. A possible reason for μ_R to be greater than μ_T may be that while determining μ_R the contact among the sliding surfaces is greater than that in the other case. The differential frictional effect would also be expected to disappear at higher loads, since in such a situation the fiber fringes would be expected to be somewhat like a fiber sheet, minimizing the effect of fiber geometry.

Variation in the Mechanical Properties Along the Length of the Cotton Fibers

Though Fransen and Verschraege[6] have reported a maximum breaking strength at the middle and a minimum value at the tip of the fibers, a true picture of the variations of the tensile properties along their length would be available only when the intrinsic strength values (duly corrected for area of cross section) are considered. The tenacity values expressed in grams per tex of the fibers would provide an estimate of this intrinsic strength.

The data obtained on the mechanical properties at three regions of the root-tip-oriented bundles of fibers belonging to model length for different cottons are given in table 7. There is a high variation in tenacity and elongation along the length of the fiber. In one case, the middle region registered a tenacity nearly twice as much as at the tip. The variation along the fiber was nearly as much as between cottons. The middle region of the fiber possessed the maximum tenacity with highest extensibility, whereas the tip region was largely the weakest with minimum extensibility. This information becomes important when it is realized that when a fiber bundle is broken with fiber ends gripped, the end parts of the fiber bundle break, leaving the midparts largely intact. Thus, the tenacity realized by such fiber bundles (as in yarns) would be much lower than the values obtained by conventional methods by which the middle of the fibers are generally subjected to tensile tests. It is interesting to note that the middle part of the fiber is endowed with the most desired tensile properties.

The difference in tenacity between middle and tip regions varied between cottons and was related to the taper of the cotton, the correlation coefficient being +0.67. This information is interesting in that as the fiber cross section became more and more uniform along the length of the fiber, the difference in tenacity values between the middle and tip regions of the fiber increased, though one would have expected a uniform distribution of strength in a fiber with uniform cross sections. The probable reason for this behavior is discussed in the next section.

Structural Variation Along the Length in Cotton Fibers

The data collected on the birefringence and crystallite orientation factors are reported in table 8.

Birefringence varied from 0.0398 to 0.0524 for the different cottons, and the tip-root differ-

TABLE 7.—*The tenacity and elongation values at three regions of fibers for different cottons*

Cotton	Tenacity (g/tex)			Elongation (%)		
	Root	Middle	Tip	Root	Middle	Tip
'Sujata'	21.1	27.2	19.8	13.2	15.0	9.4
'Gujarat 67'	14.0	15.4	14.4	12.0	11.7	11.4
'MCU 1'	11.3	17.0	11.0	8.1	9.3	8.7
'Sanjay-A'	15.4	20.3	11.0	10.9	11.0	8.2
'Digvijay'	14.0	27.4	14.4	10.5	9.4	6.1
'Sanjay-B'	15.3	20.5	11.0	10.4	11.3	8.6
'Acala'	16.2	19.1	14.1	9.4	14.3	10.2
'Koilpatti-7'	15.3	24.7	16.5	7.3	9.0	6.2
'C.J. 73'	16.9	27.1	13.3	11.9	13.4	7.0
'V-797'	10.4	20.6	9.7	9.2	10.9	6.0
'PRS-72'	13.4	16.2	10.1	7.4	13.3	7.8
'Sea Island'	15.0	19.8	12.5	12.8	18.9	11.9

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[6] Fransen, T., and Verschraege, L. Final Report of PL 480 Project No. UR-E4-(20)-1, p. 61.

ence varied from nearly 0 to 0.0081. A detailed analysis of variances revealed that the birefringence values varied not only among cottons but also among regions within a cotton. The birefringence of the cotton at the root was significantly lower than that at the tip, and there was a general increase from the root to tip. The analysis also showed that the increase in birefringence values from the root to tip was different for different cottons. The maximum difference in birefringence between tip and root regions within a cotton is found to be nearly 50% of the difference observed between cottons, which would mean that there is a considerable amount of systematic structural variation along the length of fibers.

Since birefringence is largely affected by molecular orientation, changes in birefringence could be interpreted as changes in the molecular orientation. This would mean that as molecular

TABLE 8.—*Birefringence and optical and X-ray orientation factors for the three regions of different cottons*

Cotton	Region	Refraction index		Birefringence (Δn)	Orientation factor	
		n_{11}	n_1		Optical (f_o)	X-ray (f_x)
G. hirsutum:						
'MCU 1'	Root	1.5669	1.5269	0.0400	0.646	0.590
	Middle	1.5673	1.5267	.0406	.656	.678
	Tip	1.5694	1.5274	.0420	.679	.671
'MCU 4'	Root	1.5673	1.5246	.0427	.690	.601
	Middle	1.5679	1.5247	.0432	.698	.644
	Tip	1.5718	1.5247	.0471	.761	.650
'Acala'	Root	1.5694	1.5261	.0433	.700	.675
	Middle	1.5700	1.5250	.0450	.727	.679
	Tip	1.5706	1.5254	.0452	.730	.684
'PRS-72'	Root	1.5608	1.5207	.0401	.648	.589
	Middle	1.5603	1.5205	.0398	.643	.597
	Tip	1.5612	1.5205	.0407	.658	.588
'Gujarat-67'	Root	1.5672	1.5260	.0412	.666	.562
	Middle	1.5667	1.5259	.0408	.659	.628
	Tip	1.5671	1.5261	.0410	.662	.607
G. herbaceum:						
'V-797'	Root	1.5626	1.5242	.0384	.621	.644
	Middle	1.5656	1.5240	.0416	.672	.668
	Tip	1.5701	1.5236	.0465	.751	.673
'Digvijay'	Root	1.5679	1.5267	.0412	.666	.694
	Middle	1.5689	1.5263	.0426	.688	.720
	Tip	1.5679	1.5266	.0413	.667	.686
G. barbadense:						
'Sujata'	Root	1.5726	1.5251	.0475	.767	.610
	Middle	1.5744	1.5253	.0491	.793	.699
	Tip	1.5754	1.5249	.0505	.816	.714
'Sea Island'	Root	1.5675	1.5262	.0413	.667	.597
	Middle	1.5689	1.5257	.0432	.698	.671
	Tip	1.5729	1.5263	.0466	.753	.650
G. arboreum:						
'Sanjay'	Root	1.5666	1.5239	.0427	.690	.699
	Middle	1.5681	1.5243	.0438	.708	.732
	Tip	1.5716	1.5245	.0471	.761	.749
'CJ 73'	Root	1.5707	1.5262	.0445	.719	.688
	Middle	1.5712	1.5261	.0451	.729	.718
	Tip	1.5719	1.5263	.0456	.737	.731
'Koilpatti-7'	Root	1.5690	1.5171	.0519	.838	.706
	Middle	1.5697	1.5173	.0524	.847	.737
	Tip	1.5717	1.5173	.0544	.879	.784

chains spiral from the root to the tip of the fiber, orientation steadily improves and the extent of improvement would depend upon cottons.

The data on crystallite orientation (X-ray orientation factor) show differences in the orientation values observed on the root, middle, and tip regions of the fibers. Analysis of variance revealed that the orientation at the root region significantly differed from both the middle and tip regions. It was also observed that the change in orientation values differed from cotton to cotton. On the other hand, there was no significant difference between the middle and tip regions and, in fact, in a few cases, the crystallite orientation showed even a slight decrease in the tip region as compared with that of the middle region.

Since the length and profile of a cotton fiber is fully determined during the lengthening phase of growth itself, subsequent lay of the chain molecules during the deposition of cellulose might be expected to be influenced by the geometrical features of the fiber. This profile is characterized by the taper of the fibers. For a fiber approaching a cylindrical shape, the difference between orientation at the tip and the root regions will be a minimum (fig. 3). In other words, the more cylindrical a fiber, the more uniform the spiraling of the chain molecules along the entire fiber, whether the orientation is measured by optical means or by X-ray diffraction techniques.

As shown, the orientation of both chain molecules and crystallites generally improved from root to tip, and the minimum improvement was observed in fibers with uniform cross sections. This would seem to suggest a tendency for the tensile strength to improve from root to tip, and the maximum improvement would be in fibers making a small angle at the tip. But, surprisingly, the data on the mechanical properties have shown a maximum value at the middle with relatively lower values at the ends. This suggests that in addition to molecular orientation, other structural parameters having adverse effect on tensile strength play a dominant part in the tip of the fibers. Structural reversals are already known to be sites of weakness in cotton fibers. Therefore, on a few chosen fibers, the structural reversals were studied on the root, middle, and tip parts of the fibers. The data obtained are given in table 9. It may be seen that the tip has the maximum number of reversals, and the root the minimum.

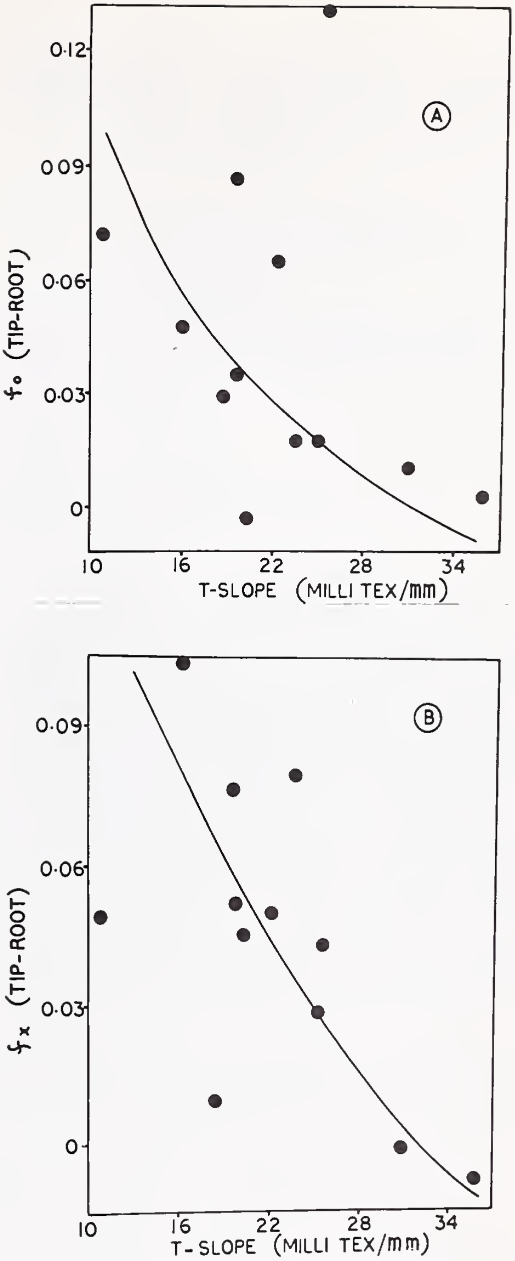

FIGURE 3.—Difference in orientation between tip and root versus fiber taper.

Thus, the tenacity values would be expected to increase from root to tip because of improvement in orientation and to decrease because of higher incidence of structural reversals. Whereas the improvement in orientation does not exceed 15%, the variation in structural reversals is about 30% to 100%. This could largely explain the drop in strength at the tip. Perhaps the determination of molecular chain length and its distribution along the length of the fiber may throw further light on this phenomenon.

TABLE 9.—*Structural reversals for the three regions of different cottons*

Cotton	Reversals per cm		
	Root	Middle	Tip
'Sujata'	19	20	29
'Koilpatti-7'	11	9	18
'Digvijay'	7	8	18
'Gujarat-67'	12	17	21
'Acala'	14	19	26
'CJ 73'	8	10	19

SUMMARY

A methodology for measuring taper has been proposed. It is suggested that fiber taper can be characterized by measurements made on the model length of the cotton. Among the fiber properties, fiber length alone seems to be related to taper, suggesting that taper could largely be treated as an independent property possibly capable of giving extra information on processing characteristics of cottons. Differential frictional effects have been observed for the cotton for the first time, and it was found that when fiber assumed a more uniform cross-sectional shape along its length, the effects of differential friction were minimal. Also, the middle part of the fiber was found to possess the maximum tenacity with highest extensibility, whereas the tip region was the weakest with minimum extensibility. An interesting observation is that as the fiber cross section became more and more uniform along the length of the fiber, the differences in tenacity values between the middle and tip regions of the fibers increased. The chain molecules became progressively better oriented as one proceeded from the root to the tip of the fibers, and this change in orientation appeared to be influenced by fiber profile. The higher incidence of structural reversals seems to be a possible factor responsible for the sharp decrease in the tenacity at the tip of the fiber in spite of the most favorable molecular orientation there.

ACKNOWLEDGMENTS

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SHRINKAGE CONTROL OF DURABLE-PRESS COTTON KNITS

By G. B. Verburg, J. G. Frick, Jr., and J. David Reid[1]

(Presented by G. B. Verburg)

Cotton knit fabrics are susceptible to shrinkage on laundering. In order to produce a fabric that will not shrink excessively (more than 3%) during laundering, a certain amount of fabric must be lost during processing as preshrinkage. This amount is greatly reduced by cross-linking. In the usual method of durable-press finishing, the knit fabric is padded with a cross-linking agent, dried, subjected to compressive shrinkage, and then cured to cross-link the fabric. Applied to circular-knitted cottons, the cross-linking can reduce laundering shrinkage from 25% or 30% to 5% or 10%, and the compaction can further reduce the shrinkage to 1% or 2%. The reduced residual laundry shrinkage brought about by cross-linking is substantial, but not sufficient for most purposes. Compaction can introduce wrinkles that are fixed by subsequent cross-linking and detract from the appearance of the fabric. This tendency increases with a greater amount of compaction and limits the reduction that can be obtained in residual laundry shrinkage.

In some instances, compaction may be applied after cross-linking with less loss of fabric in the procedure to achieve the same degree of laundry shrinkage control. However, as the resiliency of the cross-linking fabric strongly resists the action of compaction, this method may not be applicable to all knitted fabrics. It is obviously not applicable to postcured textile items.

The necessary preshrinkage after a cross-linking treatment can be induced by procedures other than compressive shrinkage. It was determined that agitation of cross-linked knitted fabrics in a slack state also produced satisfactory residual laundry shrinkage, about 3%. Four effective procedures follow:

1. Hot-wet-slack-agitation.—The cross-linked knits were agitated in 62° C water while in a slack state.
2. Cold-wet-slack-agitation.—The cross-linked knits were agitated in 30° C water while in a slack state.
3. Hot-dry-slack-agitation.—The cross-linked knits were washed and dried while held to size and then tumbled at 71° C while in a slack state.
4. Hot-dry-slack-agitation.—The cross-linked unwashed knits were tumbled at 71° C while in a slack state.

About a 3-min agitation of the slack fabric in either hot or cold water was needed to reduce laundering shrinkage to less than 3% in either the length or the width. More than 5 min in hot air was required, and unheated air (25° C) was ineffective.

This work shows that methods other than mechanical compressive shrinkage can control laundering shrinkage. These methods are efficient in that they reduce residual laundry shrinkage with relatively little loss of length, allow a balanced relaxation of the fabric so that the fabric has less tendency to change size in width or length, and remove excessive finishing agents from the fabric.

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MIGRATION OF FINISHING AGENT IN TUBULAR PROCESSING OF KNITTED COTTON FABRICS

By B. A. Kottes Andrews, J. G. Frick, Jr., and Gloria A. Gautreaux[1]

(Presented by B. A. Kottes Andrews)

Several methods have been developed for reducing migration of agent in durable-press finishing of knitted cotton tubes. Control of migration is necessary because knitted fabrics currently are processed in either of two states, open width or in the tubular form that is produced by a circular knitting machine. It is in this latter state, in which two fabric layers are processed simultaneously, that migration is most likely to occur. Localization of this migration problem among the steps of the finishing process, effects of variables in the process, as well as methods of reducing the migration are detailed in this presentation.

Patterned jerseys of 100% cotton and of cotton blended with less than 51% polyester were given durable-press finishing treatments from solutions containing 6% solids dimethyloldihydroxethyleneurea (DMDHEU). The fabrics were processed either open width or as fabric tubes, which were slit at various stages during processing so that the rest of the processing was performed on the opened tubes. Differences between fabric surfaces in resistance to a direct dye were used as an indication of agent migration normal to the plane of fabric. In fabrics containing less than 66% cotton, shade differences between surfaces of the layers of the tubes after dyeing are insignificant. At higher cotton contents there is evidence of migration of finishing agent in samples that were at least dried in tubular form. The migration then, occurs in the drying step. Further comparison of these samples shows that migration occurs equally from inner to outer surface and occurs to the same extent in each layer of the flattened tube. Standard textile properties obtained on similar surfaces are little affected by the state of the fabric during processing.

Two methods which effectively reduce agent migration in knitted fabrics involve either prewetting the fabric with water or retarding the drying step itself. The first method, which includes prepadding with water followed by an optional drying step to 50% moisture, provides complete penetration of cross-linking agent in a subsequent treatment with DMDHEU, and thus minimizes nonuniformity of distribution after migration. The second method delays drying through batching or room temperature drying following impregnation with agent, thus permitting back diffusion of the agent and reversal of migration.

Application of finishing agent from a water in organic solvent emulsion is another technique which reduces agent migration. In treatments with 3.5% and 6% DMDHEU from perchloroethylene emulsions containing 10% water, complete elimination of agent migration was achieved.

Migration is also reduced by replacing the conventional cross-linking systems that require high-temperature curing, such as DMDHEU and dimethylolethyleneurea (DMEU) catalyzed by magnesium chloride or zinc nitrate, with systems that are functional at lower temperatures. When knitted fabric tubes were finished with dimethylolmethylcarbamate (DMMC) in the mild-cure process, which uses highly active hydrochloric acid as catalyst and a combination drying and curing step at 100° C for 4 min, all fabric surfaces dyed similarly. Also, migration was not evident in samples finished with DMDHEU catalyzed by aluminum chlorhydroxide in a process using a 3-min cure at 140° C. Finished fabrics from such treatments have moisture regains higher than those from conventional treatments, indicating residual moisture sufficient for back-diffusion of agent to occur during processing. The possibility also exists that shade differences in dyeing due to agent migration are masked by the increase in dye receptivity produced in cotton cross-linked in the swollen state.

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In the course of this study, factors influencing the rate of water drying from the impregnated fabric were considered. An important factor is the surface tension of the cross-linking solution. It was found that organic additives such as poly(oxyethylene) glycols, high-molecular-weight or branched ethers, and even ethylene glycol, which decrease the surface tension of water, promote migration. Inorganic salts, on the other hand, increase the surface tension of water and hinder migration. Examples of salt additives that effectively reduced agent migration are sodium nitrate, calcium chloride, and sodium chloride. Each of these is either neutral or slightly acidic, and when used as 5% of pad bath did not reduce agent efficiency.

Increasing agent concentration in conventional treatments reduced the shade differences between fabric surfaces after dyeing. Whether this reduction is a result of reduced migration or of increased resistance to dyeing in highly cross-linked fabrics is not established. Although additives for hand improvement, such as polyacrylates, polyurethanes, and polyethylenes do not appear to increase migration, and in some cases mask the effects of migration on dyeing, none eliminates the problem.

The tendency of a knitted fabric to exhibit a migration problem depends, in part, on the fabric construction itself. When tubular jerseys of different yarn sizes and stitches per inch were treated with solutions containing 6% DMDHEU, it was noted that migration occurred to the greatest extent in the fabric of the tightest construction. Inclusion of 5% sodium chloride in the pad bath did, however, minimize migration to the same extent in all fabrics. Textile properties of the fabrics finished with this migration control process or with the process substituting aluminum chlorhydroxide as catalyst are approximately equivalent to those from conventional treatments. In fact, resistance to flat abrasion is actually improved by the aluminum chlorhydroxide method.

To summarize, migration of finishing agent occurs when knitted fabric tubes are dried in a durable-press finishing process. This migration can be successfully reduced by several techniques. Application of finishing agent to fabric with increased water content or delaying the drying step in the conventionally padded fabrics are effective, but require additional finishing operations. Application of agent from water in solvent emulsion controls migration, but requires additional equipment. Substituting low-temperature cross-linking systems offers a more feasible approach as does incorporation of salt additives in a conventional pad bath.

EASILY CREASABLE DP COTTON FABRICS

By William E. Franklin, John P. Madacsi, and Stanley P. Rowland[1]

(Presented by William E. Franklin)

ABSTRACT

Latent acid metal salts were used as activating catalysts in cotton fabrics cross-linked with dimethyloldihydroxyethyleneurea and hydroxy acids or polycarboxylic acids. These catalysts enhanced the recurability such that sharp permanent creases were formed in fully cured fabrics when they were heated at 145° to 180° C for 15 s. The activating catalysts can be added to the pad bath before the fabrics are cured or impregnated into the cured and washed fabric. Preactivation offers simplicity in processing, whereas post-activation offers better control of the cure, stability of the activated fabric, and better creasability.

INTRODUCTION

The treatment of cotton fabrics to impart wrinkle-resistant and smooth-drying properties has gained universal acceptance in the textile industry. These treatments impart desirable properties by forming chemical cross-links that bond the cellulose molecules together and thus lock the fibers in a definite configuration. One of the undesirable features of such cross-linking treatments is that new creases or flat seams cannot be formed in the treated fabrics without using processes involving chemical reactions that break the cross-links and reform them in new positions within the fibers. Such a process is called a recure if it results in a permanent change in the configuration of the fabric.

A number of approaches to the development of practical, recurable, durable-press cotton fabrics were reviewed briefly in the first paper of this series (*5*).[2] One approach involved adding a catalyst to the finished fabric before creasing (*10*). Little success was achieved with this approach because a major loss of strength occurred under the conditions necessary to produce a durable crease.

A more promising approach involves using internally catalyzed fabrics. The previous papers in this series reported the use of polycarboxylic acids (*6, 7*) and hydroxy acids (*8*) as coreactant curing catalysts with *N*-methylol cross-linking reagents. The hydroxy acids of polycarboxylic acids became bonded to the cotton cellulose during the curing step and thus deposited acidic groups in the fabric. These acidic groups were capable of catalyzing recuring reactions when the fabric was heated to form new permanent creases. Although it is possible to form sharp permanent creases in these internally catalyzed fabrics, a limitation of their use is the period of heating (5 min at 160° C) required for recuring.

The objective of this study is to provide durable-press cotton fabrics that, after curing, may be formed permanently into desirable shapes, such as sharp creases or flat seams, by conventional hand ironing or hot-head pressing. This paper describes the use of activating metal salts with hydroxy acids or polycarboxylic acids. These catalysts were used to reduce the recuring time required to form sharp permanent creases in fully cured durable-press cotton fabrics.

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[2] Italic numbers in parentheses refer to items in "Literature Cited" at the end of this paper.

MATERIALS AND METHODS

Two fabrics were used in this study, a khaki cotton twill that was commercially mercerized and weighed 7.65 oz/yd^2 and an 80×80 cotton printcloth that was desized, scoured, and bleached, and weighed 3.15 oz/yd.^{2} Dimethyloldihydroxyethyleneurea (DMDHEU) was obtained as a 45% solids solution (Permafresh 183) from Sun Chemical Co., glycolic acid (technical grade, 70%) was obtained from Eastman Kodak Co., and cyclopentanetetracarboxylic acid (CPTA) was obtained from Coastal Chemical Co. Other catalysts were reagent-grade chemicals obtained from laboratory supply houses. The softener was a 30% solids emulsion of polyethylene (Velvetol OE) from Quaker Chemical Corp., and the nonionic wetting agent was Triton X-100 from Rohm and Haas Co.

The fabric samples were treated by a pad-dry-cure process. The printcloth samples were padded to 100% wet pickup with solutions containing 8% of DMDHEU, the specified amounts of catalysts, 2% of the softener, and a trace of the wetting agent. The khaki twill fabric was padded to 70% wet pickup with solutions containing 12% of DMDHEU, the specified amounts of catalysts, 2% of the softener, and a trace of the wetting agent. The fabric samples were dried on pin frames for 8 min at 70° C, then cured under the specified conditions. The fabric samples were not laundered before testing for recurability (creasability), but were given one machine-wash and tumble-dry cycle before other physical tests.

Physical tests were performed according to the standard ASTM methods (*3*): wrinkle-recovery angle (WRA), tearing strength by the Elmendorf method, breaking strength and elongation at break by the strip method, and Stoll flex abrasion resistance. Data from all of these tests, except the wrinkle-recovery angles, are reported as percentages of those of the unmodified laundered control of the same fabric.

Durable-press appearance ratings were measured after one machine-wash and tumble-dry cycle by the AATCC method (*1*) by comparison with plastic replicas. Creasability was measured by pressing the folded, unlaundered fabric samples with a preheated hand iron that was controlled at the desired temperature from a thermocouple placed between the sides of the folded fabric. Creasing conditions were 15 s at 160° C unless otherwise specified. The creased fabric samples were opened flat, stapled to towels with the apex of the crease facing out, and subjected to five machine-wash and tumble-dry cycles. The creases that remained in the samples were rated by three observers against AATCC photographic standards (*2*) as modified by Hobart (*9*).

RESULTS AND DISCUSSION

Latent acid metal salts may be used in conjunction with carboxylic acids to provide very active catalyst systems (*4, 11, 12*). In this study, latent acid salts, termed "activating catalysts," are used with carboxylic acids that are covalently bonded to cotton fabrics containing DMDHEU cross-links. These catalyst systems provide internal catalysis of rapid recuring reactions in durable-press cotton fabrics.

Activating catalysts may be added to fabrics containing bound carboxylic acid groups in two ways: in the pad bath formulation before the original cure or by impregnation after the fabric has been cured with the carboxylic acid as the only catalyst and washed. These two methods are termed "preactivation" and "postactivation," respectively. Since there are considerable differences in the methods of applying the catalysts and in the properties of the treated fabrics, preactivation and postactivation are discussed separately.

Preactivation

In the initial experiment on preactivated, recurable, durable-press fabrics, cotton twill fabric was treated with DMDHEU, either a polycarboxylic acid (cyclopentatetetracarboxylic acid-CPTA) or a hydroxy acid (glycolic acid), and the activating catalyst (either magnesium chloride hexahydrate or zinc nitrate hexahydrate). The hydroxy or polycarboxylic acid was used in relatively large amounts (33%, based on the weight of the reagent) in order to confer a degree of permanent recurability on the fabric. The activating catalyst was used in much smaller amounts (4%, based on the weight of the reagent). Since the combination of the activating catalyst and the carboxylic acid constitutes a very active catalyst system, the curing conditions used with these formulations were milder than those used with formulations containing only the carboxylic acid. The textile and recuring properties of these fabrics are given in table 1.

The textile and strength retention properties of these fabrics are quite similar to those of fully cured, conventionally catalyzed, durable-press cotton fabrics. The wide variability in abrasion resistance among these otherwise similar fabrics is typical of fabrics treated with these highly active catalysts.

The objective of this study was to provide a fully cured durable-press fabric that would accept a crease rated 4.0 or better after five laundering cycles when creased for 15 s at 160° C. This requirement is equivalent to the formation of a sharp, permanent crease in the fabric when a hand iron adjusted to the cotton setting is passed along the crease four or five times.

Two of the three fabrics in table 1 meet this objective. All three fabrics exhibited greatly enhanced recurability over similar fabrics treated with formulations not including the activating catalyst and cured to the same level of WRA. The lower recurability of the C/Z fabric may be due in part to a lower activating ability (on a weight to weight comparison) of zinc nitrate, but the difference is greater than that usually observed in comparisons between magnesium chloride and zinc nitrate as activating catalysts.

A source of variability in these preactivated, recurable, durable-press treatments is the quality of the DMDHEU used in the formulation. Thus, the use of an old batch of DMDHEU from the same supplier, when used in the G/M formulation (table 1) resulted in a fabric with both a lower conditioned WRA (266° as compared to 305°), and a lower recurability (2.3 as compared to 4.1). This variation is in the opposite direction from that observed as a result of lower catalyst concentrations or milder curing conditions, where a lower WRA is associated with a higher recurability. These differences were not observed when the two batches of DMDHEU were used in formulations containing only the carboxylic acid catalyst or only the metal salt catalyst. All of the fabrics reported in this study were teated with the same fresh batch of DMDHEU.

Once the principle of preactivation was established it was of interest to use a number of latent acid metallic salts as potential preactivation catalysts. These salts are listed in table 2 along with the conditioned WRA's of the treated fabrics and the AATCC crease ratings of the fabrics after they were creased for 15 s at 160° C and laundered 5 cycles. All of the metal salts promoted the cure of the fabrics under the mild curing conditions used here. With the exception of aluminum chloride, all of the metal salts were about equivalent to magnesium chloride or zinc nitrate in their abilities to activate both the curing and the recuring reactions. Aluminum chloride, which is a very strong Lewis acid, caused an

TABLE 1.—*Textile and recuring properties of preactivated fabrics*[1]

Catalyst	C/Z	G/M	C/M
WRA (W+F):			
Cond. (deg.)	303	305	298
Wet (deg.)	273	279	264
Durable-press appearance	3.5	4.2	3.9
Abrasion resistance[2]	80	25	45
Breaking strength[2]	58	51	58
Tearing strength[2]	52	48	57
Recuring-Crease ratings:[3]			
130° C/15 s	0.8	2.5	2.0
145° C/15 s	1.8	3.1	3.1
160° C/15 s	3.1	4.1	4.5
160° C/60 s	4.3	5.0	5.0
160° C/60 s (washed)	0.0	0.0	0.0

[1] Khaki twill fabric padded to 70% wet pickup with 12% DMDHEU, 4% carboxylic acid, 0.5% activating catalyst, and 2% softener; dried at 70° C for 8 min, and cured at 130° C for 4 min. Catalysts: C, cyclopentenetetracarboxylic acid; G, glycolic acid; Z, zinc nitrate hexahydrate; M, magnesium chloride hexahydrate.

[2] Percentage of unmodified, laundered control.

[3] AATCC crease ratings of fabrics creased for indicated times and at indicated temperatures and then put through 5 laundering cycles.

TABLE 2.—*Activating catalysts for preactivated fabrics*[1]

Catalyst	Cond. WRA (deg., W+F)	Recurability[2]
Aluminum chloride hexahydrate	315	3.0
Aluminum chlorohydroxide	312	4.3
Ammonium chloride	302	3.6
Calcium chloride	305	4.1
Magnesium dihydrogen phosphate	296	3.5
Zinc chloride	291	3.8

[1] Cotton printcloth padded to 100% wet pickup with 8% DMDHEU, 3% CPTA, 0.5% activating catalyst, and 2% softener, dried 8 min at 70° C, and cured 4 min at 130° C.

[2] AATCC crease rating of fabric samples creased 15 s at 160° C and put through 5 laundering cycles.

overcure under the mild curing conditions used here (4 min at 130° C), as seen by the high WRA, relatively low recurability, and an 83% loss of tearing strength.

The effects of the curing conditions on the conditioned WRA and the recurability of the treated fabrics are given in table 3. The printcloth samples were treated with solutions containing 8% DMDHEU, 3% glycolic acid, 0.5% magnesium chloride hexahydrate, and 2% softener, and were dried at 70° C for 8 min before curing. The degree of recurability dropped to a crease rating of about 2.5 and leveled off as the severity of the original cure increased. The properties of the fabric cured at 130° C for 2 min indicated that a short curing time was important in retaining recurabiilty. The more severe conditions, particularly the longer curing time, might have allowed mobility of the cross-links to positions in which they were not readily broken and reformed in the recuring process.

A stability test was performed on the dried and uncured fabric treated with the same formulation as the fabrics in table 3. The conditioned WRA of the fabric increased from 242° (W+F) immediately after drying to 289° (W+F) after 90 days of storage. In the same period, the recurability crease rating of the fabric decreased from 5.0 to 4.5. During this period of storage, the recurability crease ratings of fully cured preactivated fabrics decreased by approximately one crease rating unit. Thus, preactivated fabrics are not suitable for use in delayed cure processes because of premature curing in drying and storage. On the other hand, a slow cure at low temperature does give a good balance of WRA against retention of strength and of recurability.

A series of experiments varying the concentrations of the hydroxy acid and the activating catalyst were performed in order to determine the optimum ratio of components of the catalyst system. All of the fabric samples were cured under the same conditions at 130° C for 4 min. The catalyst composition, conditioned WRA's, and recurability crease ratings of the treated fabrics are given in table 4.

TABLE 3.—*Effect of curing conditions on WRA and recurability of preactivated fabrics*[1]

Cure		Cond. WRA	Recur-
Temp. (°C)	Time (min)	(deg., W+F)	ability[2]
100	4	271	4.8
115	4	292	3.2
130	4	305	3.2
145	4	309	3.0
160	4	310	2.7
130	2	302	4.7
130	6	309	2.5
130	8	303	2.5
(3)	(3)	242	5.0

[1] Cotton printcloth padded to 100% wet pickup with 8% DMDHEU, 3% glycolic acid, 0.5% magnesium chloride hexahydrate, and 2% softener, dried 8 min at 70° C and cured under the specified conditions.

[2] AATCC crease ratings of fabric samples creased 15 s at 160° C and put through 5 laundering cycles.

[3] Dried only.

TABLE 4.—*Effects of catalyst concentrations in preactivated fabrics*[1]

Catalyst (%)		Cond. WRA	Recur-
Glycolic acid	Magnesium chloride hexahydrate	(deg., W+F)	ability[2]
4	0.5	303	3.2
3	.5	305	3.2
2	.5	304	3.7
1	.5	302	3.8
3	.1	276	2.8
3	.25	294	4.2
3	1.0	301	4.0
3	2.0	309	4.2
0	2.0	288	2.0

[1] Cotton printcloth padded to 100% wet pickup with 8% DMDHEU, the indicated amount of catalyst, and 2% softener, dried 8 min at 70° C, and cured 4 min at 130° C.

[2] AATCC crease ratings of fabric samples creased 15 s at 160° C, then given 5 laundering cycles.

These results show only small effects on either WRA's or recurabilities caused by changing the concentration of the glycolic acid. Slightly larger effects on the WRA and recurability were observed as a result of increasing the concentration of the activating catalyst from 0.1% to 2.0%. The last entry in table 4 is for a conventionally catalyzed durable-press cotton fabric. Even though the cure was mild and the catalyst remained in the fabric during the recurability test, this conventional durable-press fabric had very low recurability. Thus, the hydroxy acid or polycarboxylic acid was a necessary component in the catalyst system for these preactivated, recurable, durable-press fabrics.

The effects of the recuring conditions on the quality of the resulting crease were measured by varying the temperature and time of the recure. The results of these experiments are given in table 5.

TABLE 5.—*Recuring conditions for preactivated fabrics*[1]

Recure		Crease rating[2]
Temp. (°C)	Time (s)	
145	15	2.5
160	15	3.5
185	15	4.5
200	15	4.7
160	240	4.7
[3]160	240	2.0

[1] Cotton printcloth padded with 8% DMDHEU, 3% glycolic acid, 0.5% magnesium chloride hexahydrate, and 2% softener, and cured 2 min at 130° C. Conditioned WRA 305° (W + F).

[2] AATCC crease rating after 5 laundering cycles.

[3] Washed with distilled water before recuring.

These results are typical of many similar experiments on preactivated fabrics. For the 15-s recures, an increase of 15° C resulted in an improvement of about 1 unit in the sharpness of the permanent crease formed by the recuring process. A recure for 15 s at 200° C (at the upper limit of the cotton setting on a conventional hand iron) was equivalent to a recure of about 4 min at 160° C.

Postactivation

A second method of introducing an activating catalyst into a recurable durable-press cotton fabric is to impregnate the catalyst into a cured and washed fabric that contains cross-links from a methylol reagent and covalently bonded acidic groups. The advantage of this postactivation technique is that the original cure of the fabric is much easier to control if the activating catalyst is not present in the fabric at that stage. After the cure, the excess carboxylic acid was washed out of the fabric, leaving only the hydroxy or polycarboxylic acid which was covalently bonded to the cross-linked cellulose of the fibers. The washing step also removed any unreacted cross-linking reagent and thus reduced the formaldehyde release of the treated fabric. When the activating catalyst was added to the fabric, the strong, mixed catalyst was formed only at sites where the carboxylic acid, and presumably also the methylol cross-linking groups; were bonded to the cellulose of the fibers. Thus, the synergistic action of the carboxylic acid with the metal salt activating catalyst took place only at the sites at which the recuring reaction occurred. Since the strong, mixed acid catalyst was formed only at the sites of the cross-links, the entire fibers were not subjected to instability or strength loss on heating which is associated with strong catalyst combinations.

Two batches of khaki twill fabric were used in the postactivation studies. They were treated by a pad-dry-cure process in the pilot plant with DMDHEU, either cyclopentanetetracarboxylic acid (PCA fabric) (*7*) or glycolic acid (HA fabric) (*8*), and a softener. After they were cured, the fabrics were given a process wash with a nonionic detergent. The PCA fabric had a conditioned WRA of 299° (W+F) and the HA fabric had a conditioned WRA of 295° (W+F).

Samples of the PCA fabric and the HA fabric were impregnated to 70% wet pickup with solutions containing 1% of various activating catalysts, then dried. The fabric samples were then creased at 160° C for 15 s. The activating catalysts and the crease ratings after five launderings are given in table 6. Three of the activating catalysts gave fabrics that were very responsive to recuring, but one of these, aluminum chloride hexahydrate, caused severe tendering of the recured fabric. The fabrics treated with the other two effective activating catalysts, zinc nitrate hexahydrate and magnesium chloride hexahydrate, did not show evidence of severe tendering. On the basis of these results, a solution of 0.5%

TABLE 6.—*Postactivation catalysts*[1]

Catalyst	Crease rating[2]	
	PCA fabric	HA fabric
$AlCl_3 \cdot 6H_2O$	5.0	5.0
$Al_2(OH)_5Cl$	3.0	2.7
$CaCl_2$	4.2	3.2
$MgCl_2 \cdot 6H_2O$	5.0	5.0
$Mg(H_2PO_4)_2$	3.3	3.8
$ZnCl_2$	2.3	2.5
$Zn(NO_3)_2 \cdot 6H_2O$	5.0	5.0
None (water only)	.8	1.0

[1] Khaki twill fabric treated with DMDHEU, softener, and either cyclopentanetetracarboxylic acid (PCA fabric) or glycolic acid (HA fabric), dried, cured, washed with a nonionic detergent, padded to 70% wet pickup with a solution of 1% of the activating catalyst, dried, and creased 15 s at 160° C.

[2] AATCC crease rating after 5 laundering cycles.

of zinc nitrate hexahydrate was used in further studies of postactivation systems.

The method of applying the activating catalyst is very important in achieving successful recures with these fabrics. The catalyst solution must be allowed to penetrate the fabric thoroughly before the fabric is dried. This was best accomplished by soaking the fabric in an excess of the solution for 15 min or more, or by squeezing the wet fabric between rollers in a padding operation. A number of attempts to activate the PCA or HA fabric by spraying the catalyst solutions on selected areas of the fabric only partially activated the fabric samples.

The effects of the conditions of the recuring process were measured by creasing samples of the postactivated (0.5% zinc nitrate hexahydrate) PCA and HA fabrics under various conditions of time and temperature. The results of these experiments are summarized in table 7.

In these creasing experiments, as with the preactivated fabrics (table 5), increasing the temperature by 15° C improved the crease rating by about 1 unit. Comparison of the crease ratings for the postactivated fabrics (table 7) with those for the preactivated fabrics (table 5) shows that the postactivated fabrics accepted creases about 1.2 to 1.5 units better than the preactivated fabrics when both were creased under the same conditions.

Table 7 also includes data on a conventionally catalyzed ($MgCl_2 \cdot 6H_2O$) durable-press cotton fabric (DP fabric-conditioned WRA 301° W+F). This fabric was activated with the same 0.5% $Zn(NO_3)_2 \cdot 6H_2O$ solution as the PCA and HA fabrics. The DP fabric was also activated with a strong, mixed catalyst similar to one which has been proposed (*6*) for altering durable-press garments. Neither of the activating solutions gave satisfactory creases, even at 180° C, when used with the conventional durable-press fabric. The mixed activating catalyst caused extensive damage to the conventional durable-press fabric when it was creased for 5 min at 160° C, as seen by severe abrasion along the edge of the crease during the five laundering cycles before the crease was rated.

The loss of breaking strength caused by creasing the postactivated PCA fabric was measured. Creasing for 15 s at 145° C (crease rating 4.0) caused a 15% loss of breaking strength to 55% of that of the untreated fabric, and creasing for 15 s at 160° C (crease rating 4.8) caused an 18% loss of breaking strength. The breaks in the tests

TABLE 7.—*Recuring conditions for postactivated fabrics*

Recure		Crease rating[1]			
Temp. (°C)	Time (s)	PCA fabric	HA fabric	DP fabric	DPA fabric
130	15	2.7	3.1	0.0	1.7
145	15	4.0	4.1	0.0	1.7
160	15	4.8	4.7	0.7	2.5
180	15	5.0	5.0	1.5	3.2
160	60	5.0	5.0	1.5	3.3
160	300	5.0	5.0	2.3	4.0

[1] AATCC crease ratings of fabric samples creased under specified conditions and put through 5 laundering cycles. All fabrics were activated with 0.5% zinc nitrate hexahydrate solution. See footnote of table 6 for definitions of PCA and HA fabrics. DP fabric: same as PCA or HA fabric except that $MgCl_2 \cdot 6H_2O$ was used as the sole curing catalyst in place of the carboxylic acid. DPA fabric: same as DP fabric except that the postactivating catalyst contained 5% citric acid in addition to the zinc nitrate.

all occurred in the heated areas of the fabrics, and most of them occurred along the creases. In contrast, a durable-press fabric sample that had been activated with the citric acid and zinc nitrate catalyst lost 35% of its breaking strength when it was creased at 145° C for 15 s.

The stability of the postactivated fabrics was also measured. Samples of the PCA and HA fabrics were activated with 0.5% $Zn(NO_3)_2 \cdot 6H_2O$ solution, then stored for 200 days. At the end of the storage period, the activated fabrics retained 88% to 89% of their breaking strengths and accepted creases rated at 4.1 and 4.0 when creased for 15 s at 160° C and subjected to five laundering cycles. This stability of recurability of the postactivated fabrics contrasts to the instability of the preactivated fabrics, which steadily lose their ability to accept sharp durable creases over long periods of storage.

SUMMARY

To enhance the creasability of durable-press fabrics prepared with DMDHEU and a hydroxy acid or a polycarboxylic acid, activating catalysts can be applied either in the pad bath for the original finishing treatment to give preactivated fabrics, or by impregnation in the cured and washed fabric to give postactivated fabrics.

In the preactivation process, the catalyst mixture is very active and care must be exercised to avoid overcuring the fabric. Suitably cured preactivated fabrics may be given sharp durable creases (AATCC crease rating 4.0 to 5.0 after five laundering cycles) by pressing them with a hand iron for 15 s at 160° to 200° C. The effects of the curing conditions and the concentrations of carboxylic acid and metal salt components of the preactivating catalyst system have been studied to establish optimum conditions for producing high wrinkle-recovery angles but still retaining high levels of creasability.

In the postactivation process, the activating catalyst is applied to cured and washed fabrics having DMDHEU cross-links and carboxylic acid groups covalently bonded to cotton cellulose. The original cure in the postactivated process is easily controlled, and adding the activation catalyst has very little effect on the resilience, strength, or stability of the fabric. The creasability of the postactivated fabric is retained over long periods of storage. Sharp permanent creases are formed in postactivated fabrics when they are ironed at 145° to 160° C for 15 s, and little strength loss is caused by the creasing process.

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A DURABLE FLAME-RETARDANT FINISH FOR COTTON BASED ON THPC AND UREA

By Darrell J. Donaldson, Floyd L. Normand, George L. Drake, Jr., and Wilson A. Reeves[1]

(Presented by Darrell J. Donaldson)

One of the most widely used phosphorus compounds for imparting durable flame resistance to cellulose textiles is tetrakis(hydroxymethyl)-phosphonium chloride (THPC). Cotton has been rendered flame resistant by treatment with THPC, urea, and other nitrogenous material such as trimethylolmethylglycoluril (TMMGU) or trimethylolmelamine. Recent work has shown that the reaction of THPC with urea can be sufficiently catalyzed by sodium phosphate salts, thereby eliminating the need for reactive nitrogen compounds. This paper describes this finish and the effect of mole ratio of reactants, catalysts, and their concentration in the pad bath and time of cure on the durability of this finish, and the physical properties of the treated fabrics.

The treatment was prepared by dissolving sodium phosphate salt in the desired amount of water and then adding, in the following order, THPC, urea, NaOH (50%) if desired to adjust the pH to 6, and wetting agent. Samples were padded through the treating solution using two dips and two nips with a squeeze roll pressure adjusted to obtain a 70% wet pickup for sateen and 90% wet pickup for printcloth. Softeners are compatible with the treating solution.

Studies were made on the catalytic activity of the three sodium phosphate salts, monobasic, dibasic, and tribasic. Printcloth was padded with a 35% total solids solution containing a 1:1 mole ratio of THPC-urea and 4% of each sodium phosphate salt. The fabrics were dried at 85° C for 5 min and cured at 160° C for 2 min. Monobasic phosphate produced fabric with the lowest strength retention, 30% tearing strength and 56% breaking strength. Fabrics treated with either the dibasic or tribasic sodium phosphate formulation retained about the same tearing strength retention, 49%–53%. The breaking strength retained was 79% for the sample padded with the formulation containing the dibasic salts and almost 100% for the tribasic-treated sample.

Durability to laundering was tested in these treated fabrics. After 50 laundry cycles the samples treated with the solution containing the monobasic and dibasic sodium phosphate catalysts passed the DOC FF 3-71 flame-retardant test with the average char length not exceeding 3 inches. The sample treated with the formulation containing tribasic sodium phosphate failed the flame test after 50 laundry cycles. Review of this data showed that fabrics treated with the formulation containing the dibasic sodium phosphate salt had the most durable flame resistance with the highest strength retention. Therefore, further studies were made using the dibasic sodium phosphate salt as the catalyst in the THPC-urea flame-retardant system.

In order to find the optimum concentration of dibasic sodium phosphate required in the formulation, sateen fabric was padded with a 35% total-solids THPC-urea solution in which the phosphate salt concentration was varied from 1% to 8%. The fabrics were dried at 85° C for 5 min and then cured at 160° C for 2 min. Except for the formulation containing 1% Na_2HPO_4, all the treatments produced the same efficiency of polymer deposition. When the concentration of salt in the pad bath was increased from 1% to 6%, the breaking and tearing strength retained by the fabrics improved from 62% to 97% and from 37% to 64%, respectively. Higher salt concentrations failed to further improve the breaking and tearing strength of the treated fabrics. At a salt concentration of 6%, stiffness was imparted to the treated textile. The sample treated with the formulation containing 1% of the dibasic salt failed the DOC FF 3-71 flame test after 20 laundry cycles. All the other samples, after 50 laundry cycles, passed the flame test with char lengths of less than 2 inches. A pad bath concentration of 4% dibasic sodium phosphate gave the best combination of efficiency of reaction, handle, strength retained by the treated fabric, and durability of the finish to home laundering.

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The effect of pH on the THPC-urea system was next examined. A 35% total-solids THPC-urea formulation containing 4% dibasic sodium phosphate was used in this study. Sodium hydroxide (50% solution) was added to adjust the pH from 4.4 to 7.3. Printcloth, after drying at 85° C for 5 min and curing at 160° C for 2 min had about the same add-on, 19%–20%. Except for the sample treated at a pad bath pH of 7.3, all the samples passed the DOC FF 3-71 flame test with char lengths of 2.2 to 3.2 inches. The breaking strength retained increased from 73% to 106% as the pH of the treating solution increased from 4.4 to 6.7. Likewise, the tearing strength increased from 40% for the sample treated at a pad bath pH of 4.4 to 60% for those treated with a formulation whose pH was 6.0. Further increases above pH 6 in the bath did not improve the tearing strength. Therefore, a pad bath containing 4% Na_2HPO_4 and 4% NaOH (pH=6) imparted the most durable flame resistance to cotton textiles with the optimum physical properties.

Various mole ratios of THPC to urea were evaluated in formulations containing 4% dibasic sodium phosphate. Sateen was padded with a 3% total-solids solution in which the mole ratio of THPC to urea was raised from 2:1 to 1:2. The padded fabrics were dried at 85° C for 5 min and cured at 160° C for 2 min. The 2:1 mole ratio of THPC to urea gave the lowest add-on, 13.8%. The 1:1 and higher ratios of urea to THPC gave about the same add-on, 21%. Samples padded with the 1:1 THPC to urea passed the 3-s bone-dry test with a char length of 0.5 inches. Also, fabrics treated with a 1:1.5 mole ratio of THPC to urea passed the test, but the char lengths were about 6 inches. Samples treated with the 1:2 and 2:1 THPC to urea mole ratios passed the flame test initially but failed the test after 10 laundry cycles.

Time and temperature of drying did not affect the durability or handle of the treated samples. Curing at 160° C for 1 min was sufficient to impart a durable flame-retardant finish on printcloth and flannelette. A longer cure time of about 2 min at this temperature was needed to cure the finish on a sateen or cotton twill fabric.

This finish has been successfully applied to cotton twill and flannelette fabrics on a pilot-plant scale. The twill fabric was padded with a 35% total solids solution of THPC-urea (1:1 mole ratio) containing 4% Na_2HPO_4 and 4% (50%) NaOH to obtain about a 75% wet pickup. The fabric was dried at 85° C for 3 min and cured at 160° C for 2 min on a tenter frame. After a cold, hot, and cold water wash the sample had an 18% add-on. After 50 laundry cycles the samples passed the DOC FF 3-71 flame test with a char length of 0.5 inch. The sample retained 81% and 60% of its breaking and tearing strengths, respectively.

Flannelette was treated with a 30% total-solid solution containing Na_2HPO_4 and NaOH to obtain a 115% wet pickup. The fabric was dried and cured as the twill sample. The sample passed the DOC FF 3-71 flame test with a char length of 1 to 0.7 inch. The sample retained 93% and 70% of its breaking and tearing strengths, respectively.

In conclusion, cotton printcloth, sateen, and flannelette treated by a pad-dry-cure process with existing plant equipment, passed the flame retardant test method DOC FF 3-71 after 50 laundry cycles. The hand of these fabrics was very good. The fabrics were white after treatment and did not yellow on bleaching. The treated samples retained more than 80% of their breaking strength and from 60% to 70% of their tearing strength (a softener was not included in the formulation).

NEW OR UNUSUAL APPROACHES TO FLAMEPROOFING

By A. W. Frank, E. J. Gonzales, M. F. Margavio, S. L. Vail, and W. A. Reeves[1]

(Presented by A. W. Frank)

As part of an expanded program on the flameproofing of cotton, we have undertaken a study of several new and unusual approaches to flameproofing. This paper is a progress report on that work.

In an earlier study,[2] we showed that by using trimethylamine as the base for neutralizing tetrakis(hydroxymethyl)phosphonium chloride (THPC), the range of THPC-amide finishes can be extended to a wide variety of resin systems. Oxygen index (OI) data on cotton printcloth finished with 13 of these THPC-amide resins at 3 different concentrations showed a good correlation ($r=0.935$) between OI and the sum of the percentages of phosphorus and nitrogen, provided that only amide nitrogen was counted (fig. 1). The amides used in this study included urea, thiourea, and melamine, which are used in conventional flame-retardant finishes, and the cyclic ureas and carbamates, which are used in durable-press finishes. Although there were differences among the resins, the principal factor for determining flame resistance was the phosphorus and nitrogen content of the resin. The melamine resins fell far off the line if the ring nitrogens were counted. It is suggested that the melamine ring either survives combustion intact or is degraded to products that are inert.

Using this relationship as a guide, we have compared the relative efficiencies of various compounds containing phosphorus and nitrogen as flame retardants for cotton. Diethyl phosphoramidate, applied to cotton printcloth in combination with melamine or cyclic urea resins, gave OI values which were considerably higher than their phosphorus and nitrogen contents would indi-

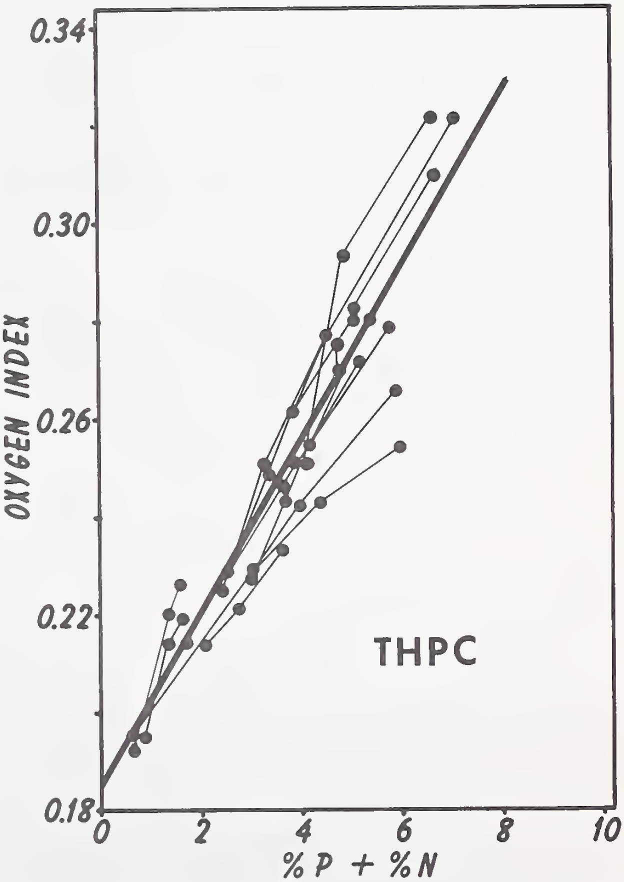

FIGURE 1.—Oxygen index (OI) versus sum of percent phosphorus and percent nitrogen in cotton printcloth treated with various THPC-amide resins.

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cate. Hexamethylphosphorous triamide, applied to cotton sateen in the absence of other resin-forming substances,[3] gave high OI values at relatively low phosphorus and nitrogen contents. These results suggest that compounds which contain phosphorus directly linked to nitrogen are inherently more efficient as flame retardants than the conventional compounds, most of which contain the P—CH_2—N link. We believe, as do others,[4] that the presence of the P—N link facilitates the phosphorylation of the cotton cellulose that precedes its dehydration.

Several inorganic complex-forming salts have been examined as flame retardants. It is reasoned that these insoluble salts are less apt to contribute to excessive stiffness than are the polymer-forming materials which are conventionally used. Also, these inorganic salts are not expected to act as added fuel in the proofed fabric or garment.

Treatment of cotton printcloth with zirconyl ammonium phosphate, followed by a melamine resin, increased the OI about 0.020 unit for each step. Durability to laundering was moderately good, and the fabric had a good, soft hand. The OI was increased even further, to 0.280, by a multiple pad-dry sequence. Simple zirconium salts, such as zirconium acetate, provided only marginal flame retardance (OI=0.253) and were not durable.

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THE EFFECTS OF DYES ON THE FLAME RETARDANCY OF COTTON FABRIC

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(Presented by Leon Segal)

INTRODUCTION

A study has been initiated for determining the effects of dyes on the flame retardancy of cotton fabric, a subject which has not been given close attention. Reeves, McMillan, and Guthrie found that aminized cotton fabric dyed with direct dyes and with acid dyes displayed different degrees of flame resistance as measured by the match test.[2] (Direct cotton dyes were considered particularly suitable in this application because the dyes and flame resistance were retained after laundering.) Flame resistance was attributed to the phosphate and sulfonate groups in the dyes. This effect was also attributed to dyestuff nitrogen in presence of the phosphate and sulfonate groups. The object of the present investigation was to determine the effects of dyes only on the flammability of all-cotton fabric. Acid dyes were applied to aminized fabric in order to extend the small amount of information available on these dyed fabrics.

MATERIALS AND METHODS

Representative dyes from the many classes of dyes were chosen as potential flame retardants on the basis of their known structures given in the "Colour Index."[3] Possible synergism with the phosphorus-based flame retardants was also a factor considered in selecting a particular dye. For this report dyes were selected from the reactive, sulfur, vat, ingrain, direct, and acid classifications and from the fluorescent brightening agents. The vat dyes included indigo dyes and a cobalt-centered phthalocyanine dye. A copper-centered phthalocyanine dye was included among the direct dyes.

Aminized fabric was dyed by the procedure described by McMillan and Guthrie.[4] Desized, scoured, and bleached cotton sateen was dyed according to procedures made available by the dye manufacturers. The level of flammability of the dyed fabrics was measured by the oxygen index (OI) technique. Thermal degradation, in a nitrogen atmosphere, was followed by thermogravimetric analysis (TGA). Dye content in the fabrics was calculated by means of the known dye structures and the results of analyses for sulfur, nitrogen, copper, cobalt, and bromine.

RESULTS AND DISCUSSION

Aminized fabric dyed with acid dyes gave the results shown in table 1. The reduction in OI is highly noteworthy, as are the lowered decomposition temperatures obtained by TGA. The thermogravimetric curves for the dyed fabrics are markedly altered from that of the undyed fabric. These data complement the match-test results and place flammability behavior of the dyed fabrics on a more quantitative basis.

Dyed cotton sateen produced the data in table 2. Dyebath concentration was varied to obtain different amounts of dye in the fabric, but equivalent dye levels for the various dyes in the fabrics were not realized. Deposition of dye was not proportional to dye concentration in the baths. Because commercial dyes are not chemically pure, the calculated dye content is necessarily in some degree of error.

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[2] Reeves, W. A., McMillan, O. J., Jr., and Guthrie, J. D. 1953. Chemical and physical properties of aminized cotton. Text. Res. J. 28: 527–532.

McMillan, O. J., Jr., and Guthrie, J. D. 1954. Process for making flameproofed dyed aminized cotton fabric. U.S. Pat. No. 2,695,833.

[3] The Society of Dyers and Colourists, Bradford, England, and The American Association of Textile Chemists and Colorists, Lowell, Mass. 2d ed., 1956.

[4] Cited in footnote 2.

Changes in OI were modest but significant. Oxygen index seemed to fall into two groups, 0.181–0.188 and 0.193–0.197, but there was not any clear-cut pattern for OI relative to dye level, dye type, or decomposition temperature.

Thermal degradation of the dyed fabrics in the absence of oxygen presents a more consistent behavior according to decomposition temperatures taken from TGA curves. The reactive dyes and the brominated indigo dye shifted the path of decomposition markedly, but the rest of the dyes in table 2 had slight effect. This effect of the two dye types is in keeping with current theories on flame retardancy. The reactive dyes are chemically attached to the cellulose molecule at the hydroxyl groups by covalent bonds; this chemical modification, then, would be expected to influence the formation of levoglucosan. The indigo dye is not chemically bound, but the flame-retardant effects of bromine are well known.

TABLE 1.—*Flame-retardant properties and dye contents of aminized fabric dyed with acid dyes*

Dye	"Colour Index" name	Oxygen index	Decomposition temperature (°C) Onset	Decomposition temperature (°C) Completed	Percent add-on
Undyed		0.195	332	382	None (0.65% N, DS = 0.08).[1]
Kiton Fast Red 3GLL.	Mixture of Acid Red 1 and Acid Red 37.[2]	.277	263	(3)	10.0 (1.85% S).
Kiton Fast Red G.	Acid Red 1	.277	256	(3)	7.5 (1.66% S).
Nyanza Fast Red BL.	Acid Red 37	.270	258	(3)	7.1 (1.59% S).
Sateen treated with 35% THPOH, NH_3 cure.		.299	303	323	5.37% P.

[1] DS = Degree of substitution.

[2] Commercial product; proportions unknown.

[3] No linear portion on curve for extrapolation.

TABLE 2.—*Dye contents and flame-retardant properties of dyed cotton sateen*

Dye	"Colour Index" name	Percent dye in — Bath	Percent dye in — Fabric[1]	Oxygen index	Decomposition temp. (° C) Onset	Decomposition temp. (° C) Complete
Undyed		..	...	0.191	363	403
Procion Rubine HBS (contains Cu).	Reactive Red 14	5	2.8	.188	322	365
Do	do	10	3.4	.188	318	364
Procion Yellow HAS (no copper).	Reactive Yellow 3	5	2.7	.193	326	345
Do	do	10	4.2	.195	332	377
Procion Rubine MBS (contains Cu).	Reactive Red 6	5	1.6	.186	319	368
Do	do	10	2.1	.191	313	368
Procion Yellow MRS (no copper).	Reactive Yellow 4	5	2.1	.188	321	365
Do	do	10	3.2	.194	326	355
Sodyesol Liquid Brown AFCF.	Sulfur Red 5	5	(0.17% S)	.184	343	387
Do	do	20	(0.50% S)	.188	343	393

TABLE 2.—*Dye contents and flame-retardant properties of dyed cotton sateen*—Continued

Dye	"Colour Index" name	Percent dye in —		Oxygen index	Decomposition temp. (° C)	
		Bath	Fabric[1]		Onset	Complete
Ponsol Khaki 2GD.	Vat Green 8	5	.97	.188	360	402
Do	do	20	1.94	.191	362	401
Blancophor SV	Fluorescent Bright	5	(0.19% S)	.195	350	392
Do	Agent 25	10	(0.25% S)	.193	352	394
Leucophor B	Fluorescent Bright	5	(0.21% S)	.193	355	394
Do	Agent 32	10	(0.21% S)	.195	348	389
Algol Brilliant Blue 4GP (cobalt-centered phthalocyanine).	Vat Blue 29	5	.2	.181	355	397
Do	do	20	1.2	.185	359	403
Chlorantine Fast Turquoise VLL (copper-centered phthalocyanine).	Direct Blue 86	5	.98	.193	358	404
Do	do	10	1.40	.197	358	406
Indigo Pure BASF	Vat Blue 1	7	.6	.186	354	396
Do	do	14.4	....	.195	357	411
Algosol Blue 06B (pentabrominated indigo).	Solubilized Vat Blue 9.	1.0	2.0	.181	330	387
Do	do	72.8	16.4	.197	304	350
Sateen treated with 35% THPOH, NH_3 cure, 5.37% P.	do	....	....	.299	303	323

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[1] Data in parentheses are elemental analysis because structure of dye not specified.

AN EFFECTIVE AMMONIA REACTOR FOR THE CONTINUOUS PRODUCTION OF FIRE-RETARDANT COTTON FABRICS

By R. M. Perkins, T. A. Calamari, H. B. Moore, S. P. Schreiber, and A. S. Cooper, Jr.[1]

(Presented by R. M. Perkins)

INTRODUCTION

The THPOH-NH_3 process for producing fire-resistant cotton fabric is particularly attractive for the treatment of lightweight fabrics because of the good hand and because of no reduction in breaking strength (*1, 2*).[2] Basically, the process involves a pad, dry, chemical cure, oxidation, wash, and dry sequence. Drake et al. (*6*) reported an interesting variation in which the heat-drying step was eliminated. Contact with the NH_3 causes immediate dehydration of the fabric and reaction with the tetrakis(hydroxymethyl) phosphonium hydroxide (THPOH). The technique of chemically drying and curing the THPOH in cotton with anhydrous NH_3 at room temperature was thus shown to be feasible. Flow rate and time of flow, as well as the water content of the wetted fabric and accessible surface area of the yarns in the fabrics, were found to be factors in the end results obtained (*6*). An extension of that study presented at the 12th Cotton Utilization Conference stated that THPOH-impregnated cotton sateen could be effectively ammoniated on a continuous basis with NH_3 flow rates as low as 1.0 l/min and ammoniation times of 3 s (*7*). The basic THPOH-NH_3 process is being followed commercially, and at least some fire-retardant fabrics marketed under the trademark Fire-Stop are being finished with this chemical-cure technique (*5*).

This paper describes laboratory experiments in which the ammoniation took place at temperatures ranging from 15° to 80° C. The effect of the NH_3 temperature on polymer formation and distribution was observed. As a result, a vertical reactor for applying hot NH_3 was designed and constructed, and is being used in a pilot-plant application of the THPOH-hot-NH_3 finish. Some processing variables are reported.

LABORATORY STUDY

Methods and Materials

NH_3 was forced into and through THPOH-impregnated fabric. For this, a small apparatus was assembled so that air could be optionally mixed with the NH_3 at a measured flow rate before the gases entered a heat exchanger, and the flow of the mixed gases could be measured before entering the reaction chamber. The gases entered the reaction chamber (a cylinder about 6 inches in diameter and 13 inches high) at the base and flowed upward through a sintered glass plate and one-half of an inch of glass beads. The THPOH-impregnated fabric was clamped in 7-inch wooden embroidery hoops and placed on the top of the reactor where the gases were forced into and through the fabric. A stainless-steel cylinder was placed on the top of the fabric to help keep it pressed closely against the reaction cylinder. The cylinder was open at the bottom and closed at the top except for a 1-inch hole in the center. The samples were immediately washed, dried, and then dyed with Kiton Pure Blue V to determine uniformity and location of polymer deposit (*8*). This is an acid wool dye which colors the polymer and not the cotton. This dyeing must be done before the oxidation because, since it is less basic, the oxidized polymer offers dye resistance. (See fig. 1.)

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[2] Italic numbers in parentheses refer to items in "Literature Cited" at the end of this paper.

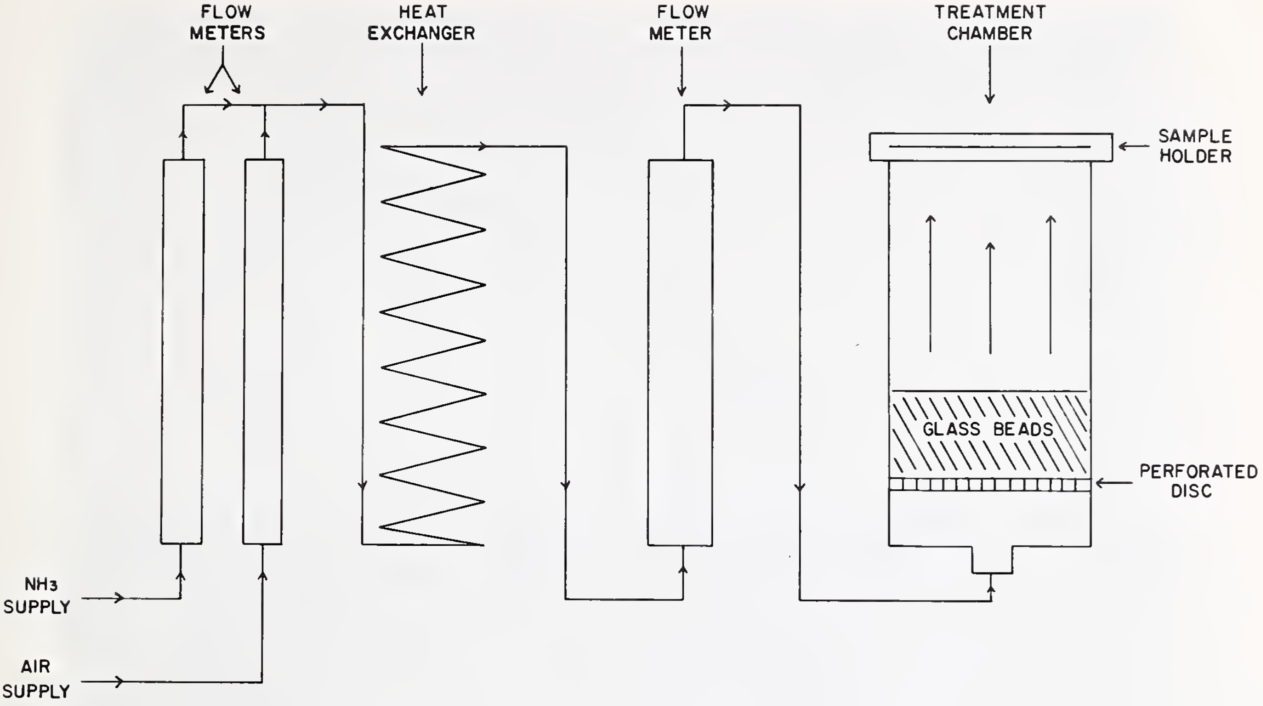

FIGURE 1.—Schematic drawing of laboratory apparatus to ammoniate THPOH-impregnated fabric.

The THPOH solutions were prepared according to the established method (*8*), which consists of the addition of cold aqueous NaOH to cold aqueous tetrakis (hydroxymethyl) phosphonium chloride (THPC). The temperature should be kept about 20° C throughout the addition. Neutralization is considered complete when the solution pH reaches 7.0–7.5. This requires a mole ratio of NaOH: THPC of about 0.9: 1.0. The samples were then dried in an electric oven on pin frames at 185° F for various periods of time to give a range of moisture. Some samples were not dried prior to ammoniation.

With 60 lb in^{2}g on both the NH$_3$ cylinder and the air and a flow rate of 1.7 ft^3/min, good comparative results were possible. That is, some treated samples dyed uniformly with the Kiton dye, some nonuniformly, and others hardly at all, indicating no reaction. Of particular interest were the differences in polymer formation (*1*) within the innermost circle, where the fabric was held across the top of the reactor and the gases were forced against or through the fabric or both, (2) outside that inner circle, but inside the embroidery hoops, where the gases escaped horizontally out of the reaction chamber but were in close contact with the fabric to react after diffusion, and (3) outside the embroidery hoop, where the gases were diluted with the surrounding air, but still reacted after diffusion. (See fig. 2.)

For the laboratory studies, printcloth samples were padded on a two-roll padder at a speed of about 2 yd/min with a solution containing 40% THPOH to an 80% wet pickup. The samples were then dried at 185° F for 2 min, 45 s, 20 s, or not at all, so that moisture ranged from about 0% to 50%. These were then exposed to NH$_3$ or NH$_3$ plus air for 15 s and immediately quenched with cold water.

Results

Room-Temperature Gas.—Dyeings showed spotting in the innermost circle for samples dried for 2 min, but almost none for samples dried for 45 or 20 s. The areas outside the innermost circle were uniformly colored. The samples that had not been predried were all poorly reacted.

Spotting was more severe when air was mixed with NH$_3$. When the exposure time was doubled to 30 s, the general pattern remained the same; however, as more polymer formed, spotting decreased. (See fig. 3.)

In another series of samples, the time of exposure to the NH$_3$ was increased up to 3 min, and some of the samples (after removal of embroidery hoops) were then held in polyethylene bags

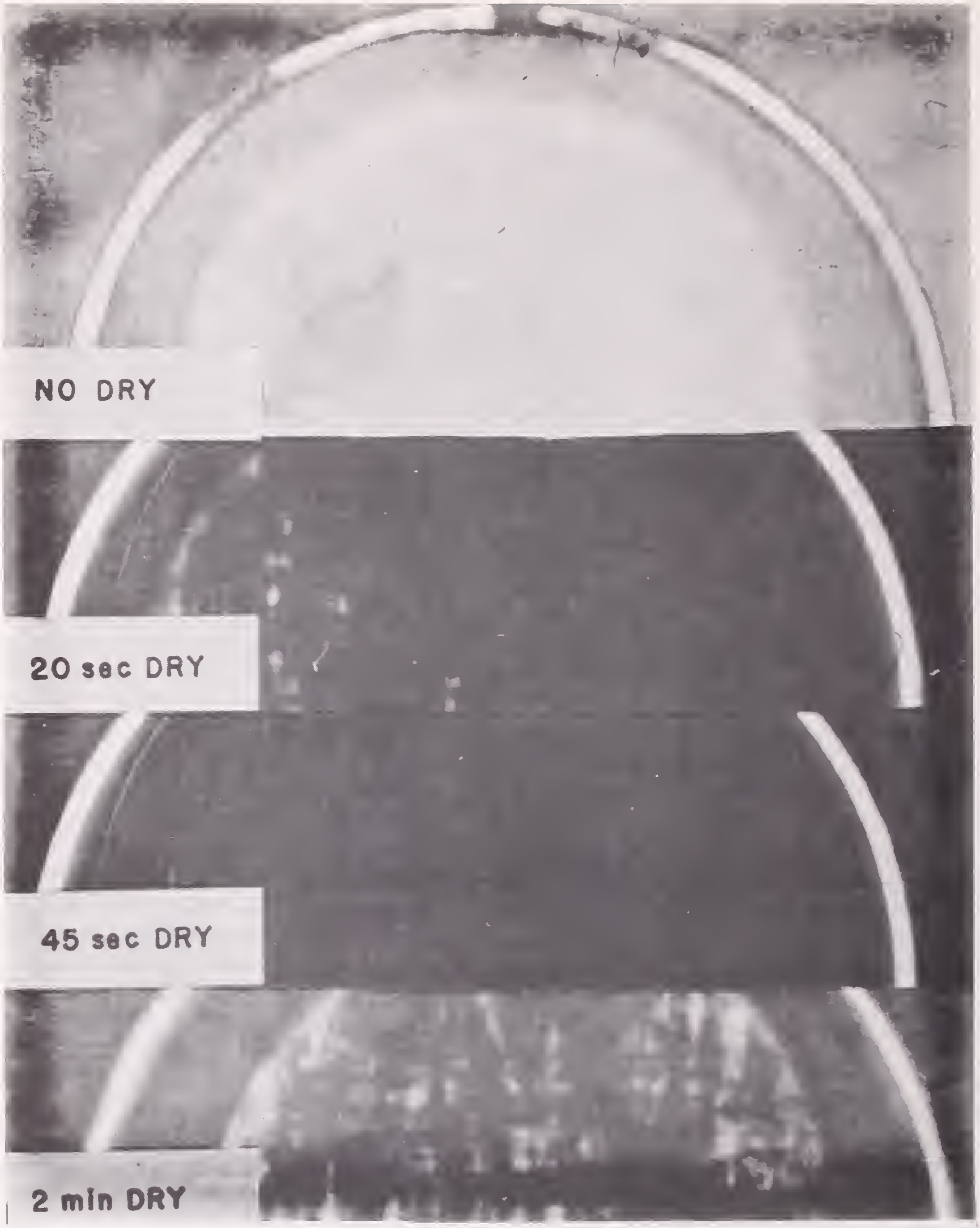

FIGURE 2.—Polymer distribution in samples treated with THPOH-NH_3 (room-temperature NH_3).

for an added hour before washing. The spotting pattern was again apparent in some of the samples in the forced-gas areas. However, when these samples were allowed to further react in the polyethylene bags with only the NH_3 absorbed on the fabric, the entire sample became uniformly colored—including the area where the embroidery hoops normally prevent reaction. (See fig. 4.)

Cooled Gas.—The effect of cooling the reaction gases was studied. Samples were padded and dried as before. The temperature of the NH_3 alone was 20° C and of the NH_3 plus air, about 15° C. Polymer formation and distribution was

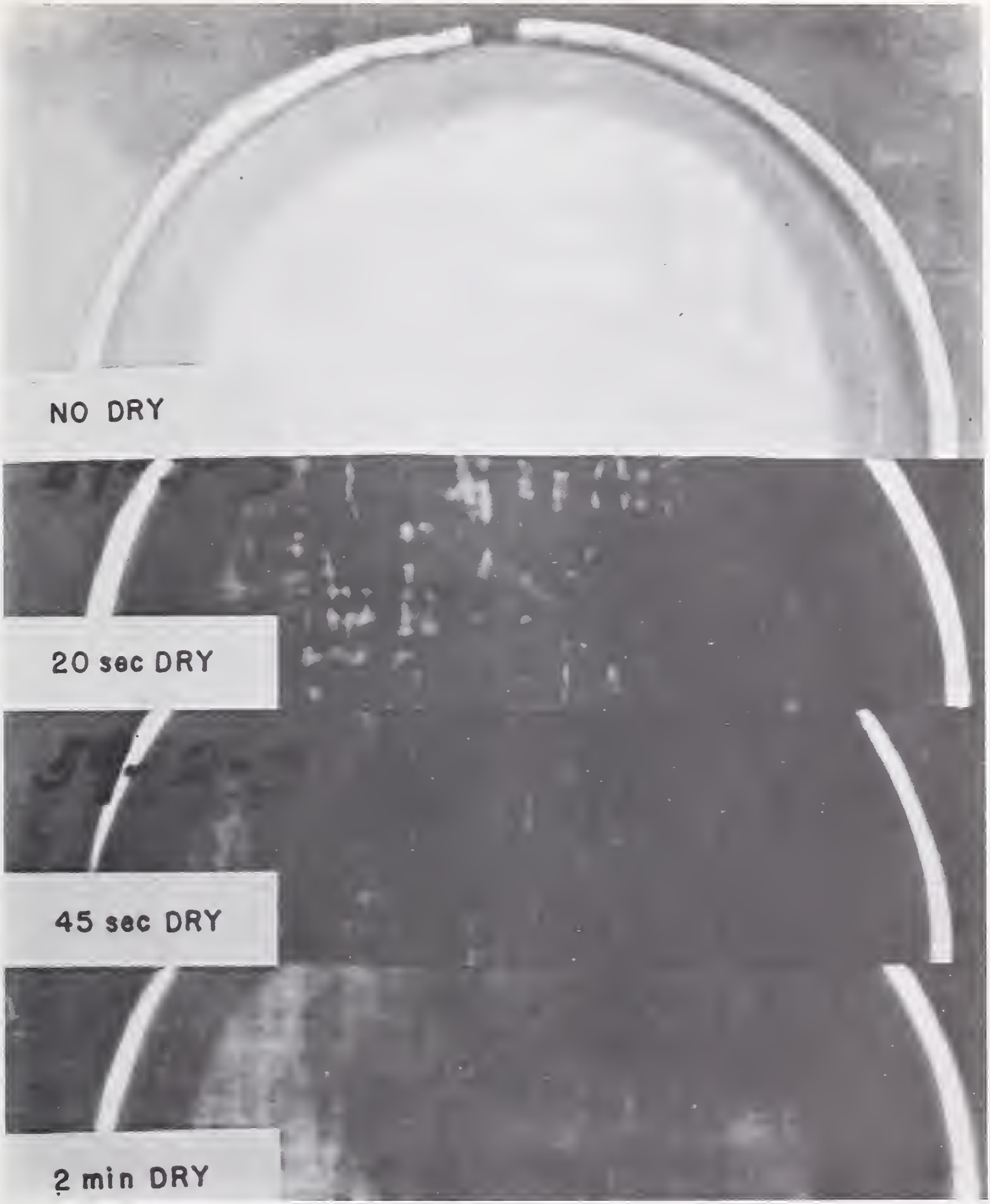

FIGURE 3.—Polymer distribution in samples treated with THPOH-NH_3 (room-temperature NH_3) plus air.

not quite as good as with the room-temperature reaction, so the cooling procedure was abandoned.

Heated Gas.—Heating the gases to 70°–80° C was tried. Conditions prior to ammoniation and quench were the same as for the cooled and the room-temperature gases. All the samples dyed uniformly (except the ones not predried). Polymer deposition was about equal in the diffused and the forced-gas areas. There was also less difference among samples predried over the range of 20 s to 2 min, with perhaps some indication of overdrying at 2 min as evidenced by reduced polymer formation. (See fig. 5.)

The addition of air appeared to be somewhat

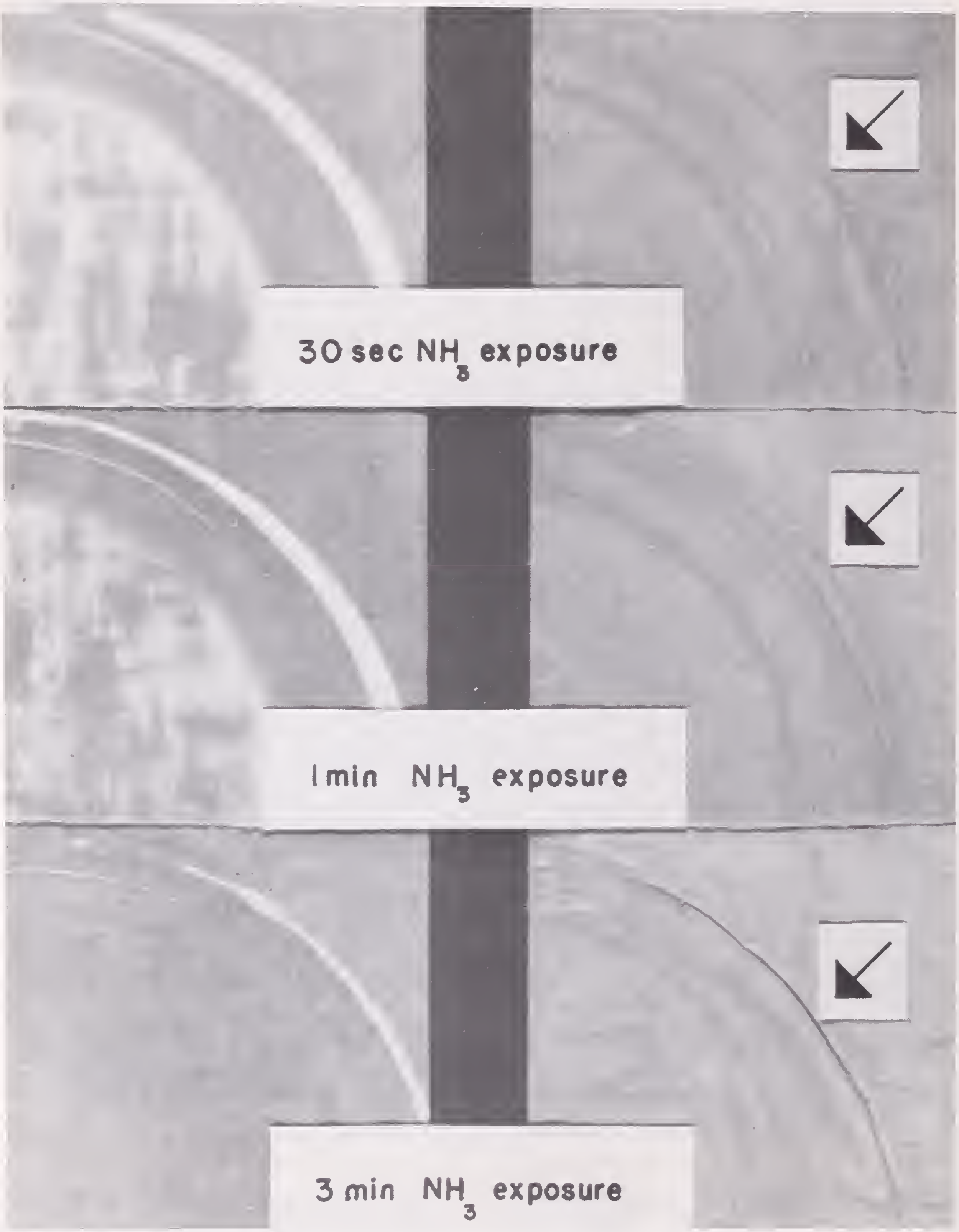

FIGURE 4.—Effect of additional dwell time after ammoniation on polymer distribution in samples treated with THPOH-NH_3 (room-temperature NH_3). *Left,* immediate rinse; *right,* 1-hour dwell time before rinse.

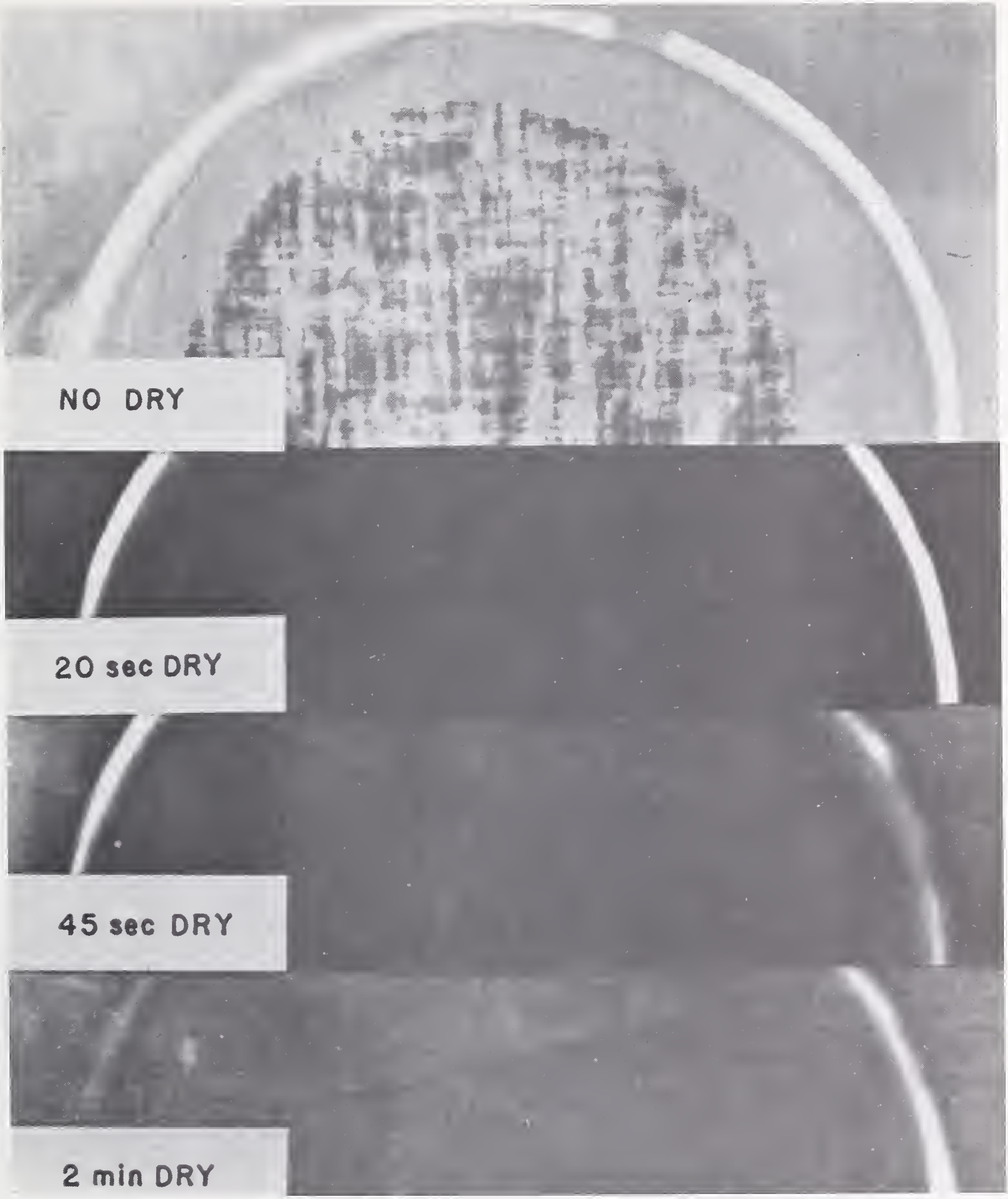

FIGURE 5.—Polymer distribution in samples treated with THPOH-NH_3 (hot NH_3).

helpful, causing less spotting, as seen in figure 6.

Overall, then, heating the reaction gases (NH_3 alone or NH_3 plus air) appeared beneficial because NH_3 exposure time to get uniform polymer formation was less than when the NH_3 was at room temperature. Forcing or diffusing the gases became equally effective for polymerization at a 15-s exposure to hot NH_3 in much the same manner that longer reaction time results in even polymer distribution at room temperature. Samples that had not been predried were all poor.

PILOT PLANT

Because laboratory tests demonstrated that using heated NH_3 in the THPOH-NH_3 process was desirable, it was believed that heated NH_3 would also be advantageous in a continuous pilot-

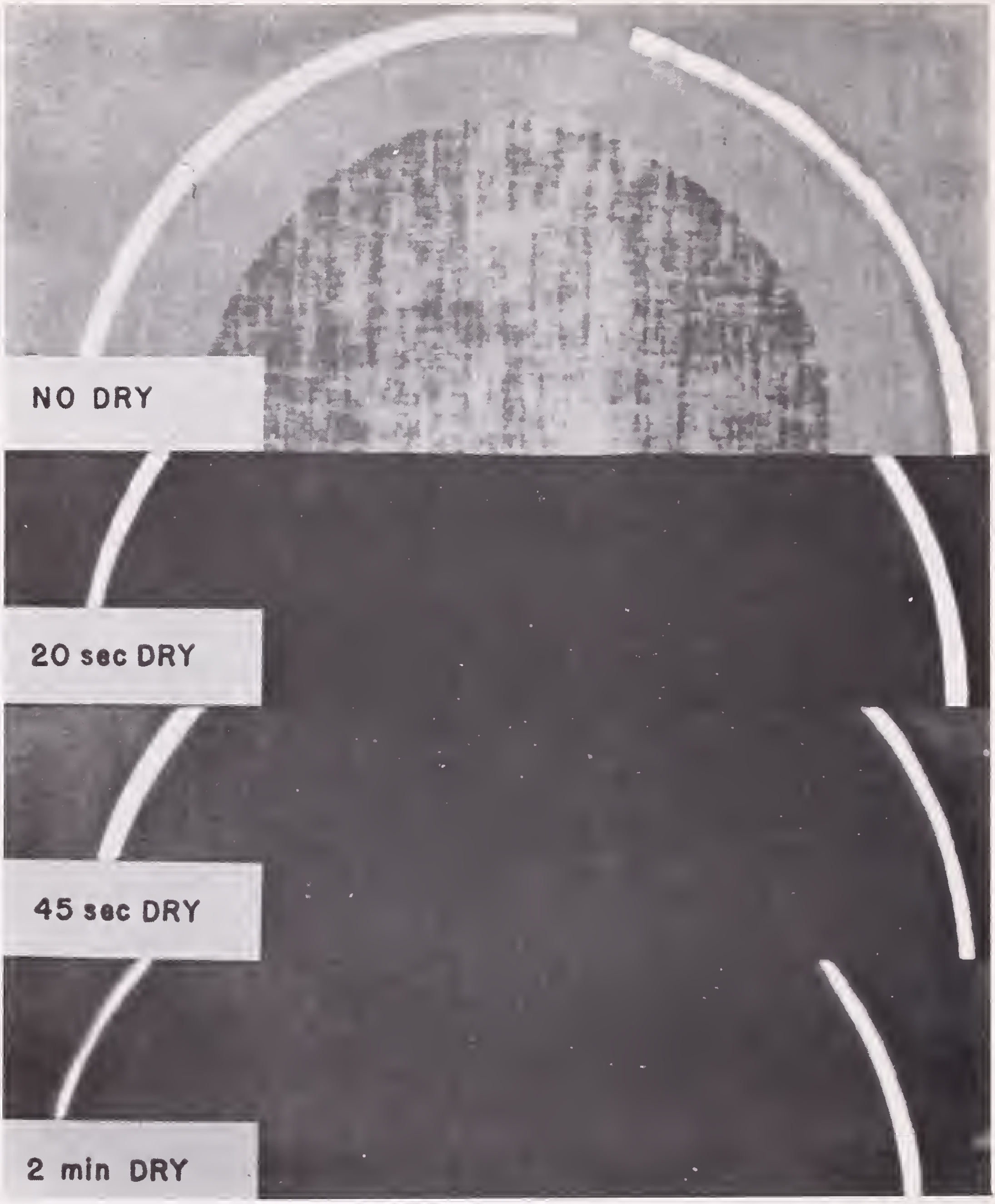

FIGURE 6.—Polymer distribution in samples treated with THPOH-NH_3 (hot NH_3) plus air.

plant process. A half-width Benz range was used for the development study. A vertical ammonia-gas reactor was designed and constructed and was positioned just beyond the drying oven (figs. 7 and 8).

The reactor consists of a reaction chamber, which is 6 ft tall, 18 inches wide, and about 1 inch thick between the wall faces. These walls are made of corrugated, fiberglass-reinforced plastic which helps keep the gas turbulent. Just outside the chamber are steam-heating tubes which keep the reaction chamber at the desired temperature. There is insulation between the reaction chamber and the outside hardboard walls. Fabric enters the reactor at the bottom and travels vertically between and against the slotted pipes to

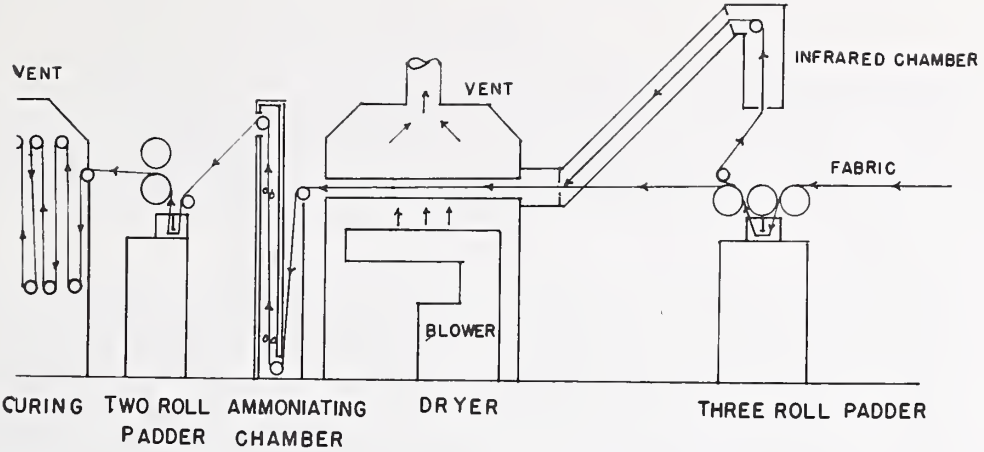

FIGURE 7.—A continuous range for THPOH-NH_3 processing (one-half).

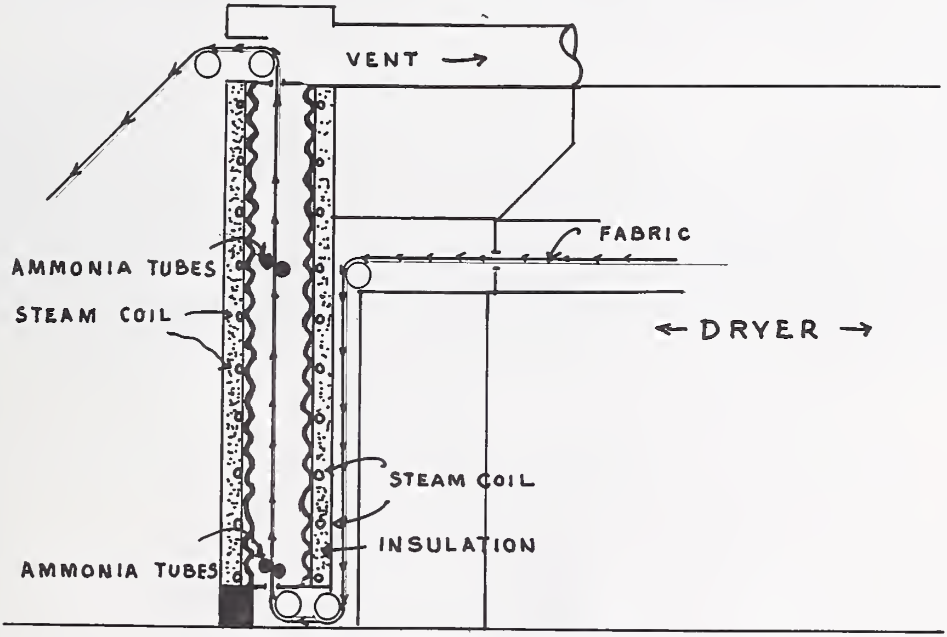

FIGURE 8.—The new NH_3 reactor.

exit at the top. The NH_3 gas is heated in a steam heat exchanger before entering the reaction chamber through the slotted pipes, horizontally positioned along the 18-inch width. An exhaust above the reactor removes the byproducts. The gas flow was measured under pressure at room temperature.

Efficiency of Old Versus New Reactor at Room Temperature

Printcloth which had been padded with 40% THPOH and dried on the tenter frame for 45 s at 145° F was ammoniated in the new reactor for 40 s at room temperature. This sample was compared with fabrics that had been treated by the old ammoniation equipment (*6*), consisting of a modified open-width washer that had been enclosed and vented (fig. 9). The NH_3 was forced through two pairs of slotted pipes, so arranged that the slots were in intimate contact with the fabric as it proceeded through the reactor. (See section AA.) Two oscillating fans were mounted in the top of the reactor to circulate the NH_3. A minimum of 3 min of ammoniation was needed for good durability when the old reactor was used, but only 40 s in the new (table 1). Theoretically, only 1 mole of NH_3 is needed to react with each mole of THPOH. In the above example, the mole ratio was about 50 to 1 of NH_3 to THPOH with the new reactor and several hundred to 1 with the old equipment.

TABLE 1.—*Comparison of samples ammoniated at room temperature in the new reactor with those ammoniated in the old reactor*[1]

Reactor	Time of NH_3 exposure (min:s)	Phosphorus (%)	Nitrogen (%)	Results of VFT after No. launderings	
				0	50
New	0:40	5.4	2.5	P	P
Old	5:00	4.4	2.2	P	P
Old	3:00	4.2	2.0	P	P
Old	1:30	3.4	2.7	P	F

P=passed. F=failed. VFT=vertical flame test (*9*).

[1] Printcloth padded with 40% THPOH, dried 45 s at 145° F.

Room Temperature Versus Hot NH_3

The next step was to compare results from room-temperature-NH_3 and hot-NH_3 treatments in the new reactor. Flannelette was padded with 35% THPOH to about 100% wet pickup, dried on the tenter frame at 145° F for 0.5, 2, or 4 min (which corresponded to moisture contents of 4%–15%) and then ammoniated at room temperature or at 200° F. The moles of THPOH/min were dependent upon the fabric speed through the reactor; the moles of NH_3/min were controlled by the pressure and the temperature of the NH_3 and measured by the flow meters.

Samples shown in figure 10 were dried for 4 min. The top pair was ammoniated for 10 s at a mole ratio of NH_3 to THPOH of about 3.5:1. At room temperature the dyeing showed polymer deposit only where the NH_3 entered the reactor and not across the whole 17-inch width of the fabric. This flow was at 0.8 ft³/min or 4-1/4 mol/min. At this low flow rate, the NH_3 was not evenly distributed across the width. When the gas was heated, the polymer distribution became more even across the width of the fabric. Likewise, keeping the fabric speed consistent (10-s ammoniation), but increasing the flow to about 2.7 ft³/min or 14-1/2 mol/min (a mole ratio of 12:1) resulted in even polymer distribution, at both room and high temperature, as seen in the middle pair of samples. The lowest pair was ammoniated for 30 s (3 times as long as the above) with a flow of about 0.6 ft³/min or 2-1/2 mol/min at a mole ratio of 6:1. The top sample was unevenly reacted, the bottom evenly. This illustrates the advantage of heating the gas, when ammoniating at low flow rates and at low mole ratios of NH_3 to THPOH. The uneven distribu-

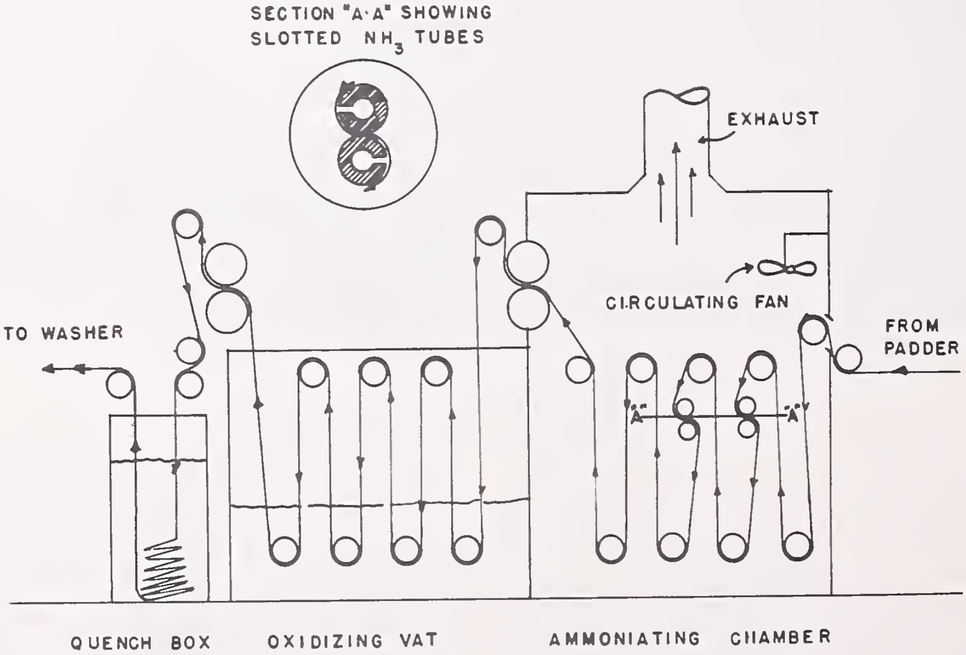

FIGURE 9.—The old NH_3 reactor.

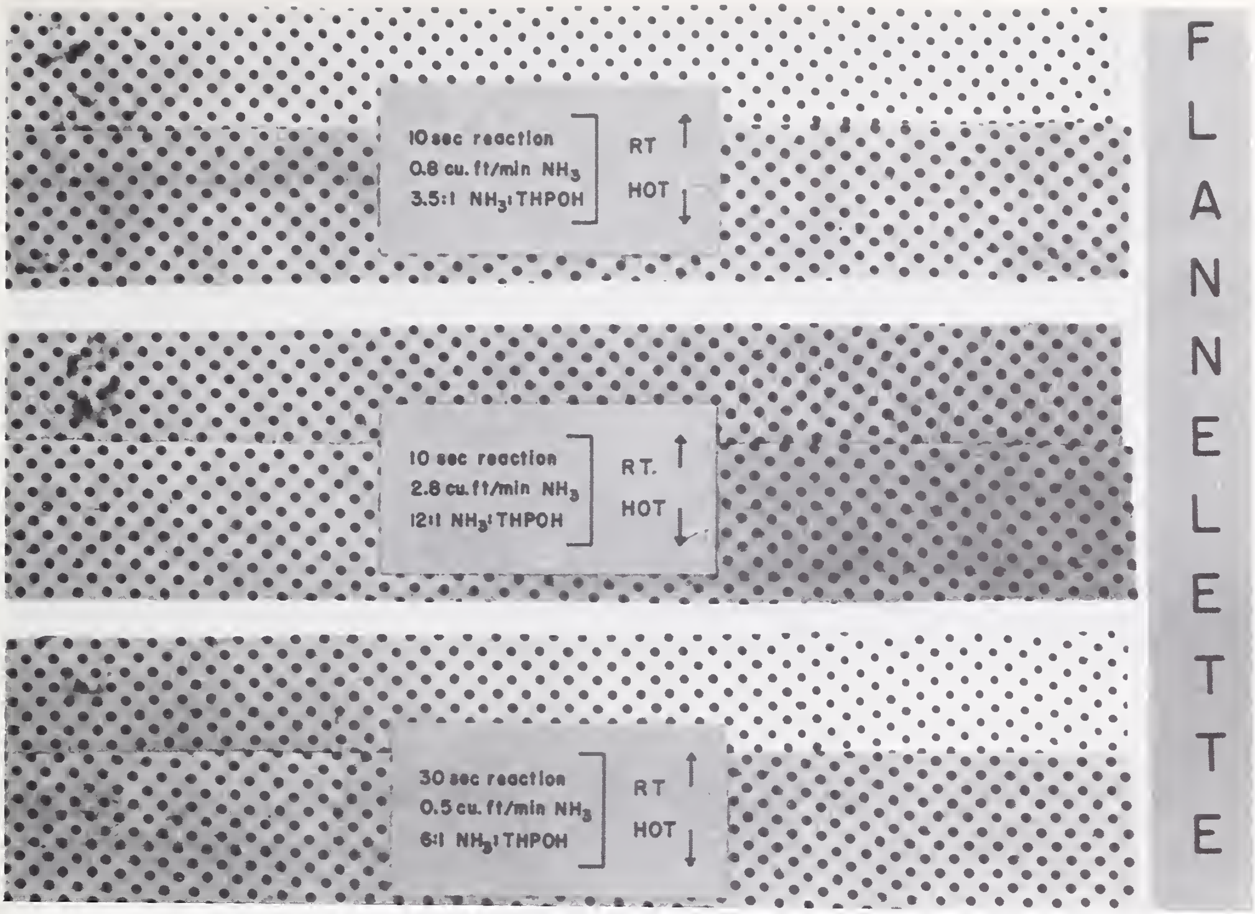

FIGURE 10.—Influence of hot NH_3 on polymer distribution in flannelette treated with THPOH-NH_3.

tion of polymer formation was apparent over the entire drying range, under the same conditions of ammoniation.

Similar experiments were done on printcloth instead of flannelette. The advantage of using hot NH_3 over room-temperature NH_3 was not as noticeable as with the flannelette. However, when a lightweight tubular knit fabric was ammoniated with room-temperature or hot NH_3, the difference was pronounced, as shown in figure 11. Drying and ammoniation conditions were the same for each sample, except for the temperature of the ammonia. The sample ammoniated at room temperature had less than 1% P, whereas that ammoniated with hot NH_3 had more than 3% P.

Influence of Flow Rate and Reaction Time on Durability

Although elemental analyses can give a good estimate of polymer formation, they cannot always predict durability. One condition which affects durability is difficult to explain; it appears to depend upon the reaction time and flow rate.

A lightweight sheeting was padded with 40% THPOH, dried for 45 s at 145° F on the tenter frame, then ammoniated at about 80° C. The ammonia flow ranged from 0.34 ft^3/min to 2.7 ft^3/min (1.8 mol/min to 14.5 mol/min). Exposure time to NH_3 ranged from 5 to 40 s. Some data are presented in table 2. Examination of the first four samples indicates that good durability can be had with a sample having initially 3.5% P and 1.3% N and exposed to NH_3 for 20 s. The mole ratio of the NH_3 to THPOH was at least 7:1. When the exposure time was doubled to 40 s and the NH_3 flow reduced about one-half in sample No. 5 versus sample No. 2, essentially the same results were found—the fabric had good durability. However, sample No. 6 with essentially the same amount of P and N and the same mole ratio of NH_3:THPOH (6:1) failed. The NH_3 flow was 14.5 mol/min, but the exposure time was only 5 s.

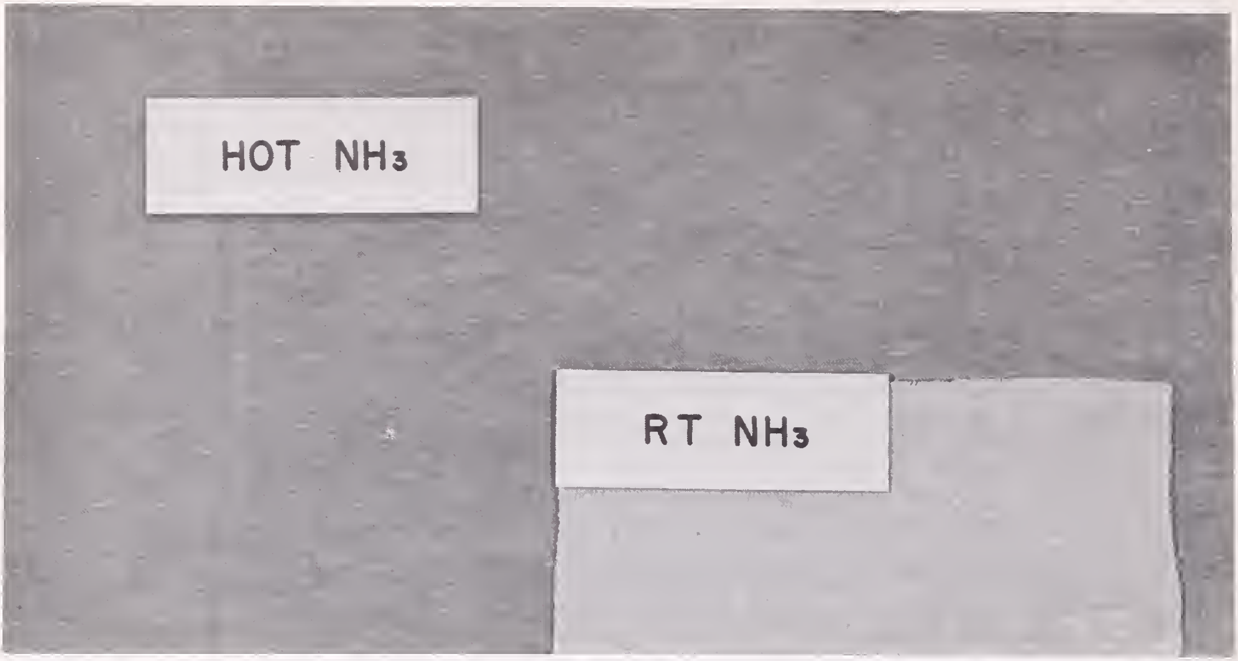

FIGURE 11.—Effect of hot NH_3 on polymer formation in knit fabric treated with THPOH-NH_3.

TABLE 2.—*Influence of mole ratio of* NH_3 *to* THPOH, *and of reaction time and flow rate on durability of* THPOH-hot-NH_3 *finish*[1]

Sample No.	NH_3 flow[2] (mol/min)	Time of NH_3 exposure (s)	Phosphorus (%)	Nitrogen (%)	Results of VFT after No. of launderings: 0	Results of VFT after No. of launderings: 50	Mole ratio of NH_3:THPOH
1	4.2	40	3.6	1.5	P	P	14:1
2	4.2	20	3.5	1.3	P	P	7:1
3	4.2	10	2.9	1.1	P	F	3.5:1
4	4.2	5	2.3	.8	P	F	2:1
5	1.8	40	3.1	1.0	P	P	6:1
6	14.5	5	3.3	1.2	P	F	6:1

P=passed. F=failed. VFT=vertical flame test (*9*).

[1] Lightweight sheeting padded with 40% THPOH dried for 45 s at 145° F.

[2] 5.25 mol/ft^3 under conditions used.

A similar situation occurred with flannelette. Both samples were treated identically except that one was ammoniated longer than the other. Essentially both samples had the same amount of polymer deposit, yet the one ammoniated longer passed the Children's Sleepwear Standard (*4*) after 50 cycles but the other passed only the vertical flame test (*9*). Initially both had about 5.6% P and 2.3% N. The sample exposed longer to NH_3 retained 84% N after 50 washes, whereas the other retained only 69%.

Preliminary laundry studies with chlorine bleach in the wash water indicate no improvement when the THPOH-NH_3 finish is formed using hot NH_3 rather than room-temperature NH_3.

Addition of Air to NH_3

The addition of air to the NH_3 did not assist the polymer formation but, apparently, by diluting the reacting mixture, decreased the efficiency of the reaction. For example, at an NH_3-to-THPOH mole ratio of 7:1, an ammoniation time of 20 s, and a gas temperature of 80° C, the addition of an equal or greater amount of air than of NH_3 caused a slightly lowered fixation of polymer on lightweight sheeting and reduced durability, as shown in table 3. This was somewhat contrary to laboratory results in which it appeared that the addition of air may have been beneficial because of added turbulence.

Effect of Drying

A 240-yd (17-inch width) roll of flannelette was padded to a wet pickup of about 100% with a solution containing 35% THPOH. The roll was dried on the tenter frame at 150°, 200°, 260°, or 320° F for various periods of time, from 15 s to 2 min. The percentage of water, as measured by the method of Berni et al., ranged from 2.1% to 15.2% (*3*). Ammoniation took place at about 80° C for 20 s. The mole ratio of NH_3 to THPOH was again 7:1. A higher mole ratio was also selected for some samples to determine whether or not this increase in NH_3 could compensate for drying inadequacies and thereby increase the durability so that the samples would pass the DOC test. Some data appear in table 4. At each drying temperature, there were samples that had initial fire resistance. adequate to pass either the DOC test (*4*) or at least the VFT (*9*). The one exception was the sample dried at 320° F for 1 min (2.3% H_2O) whose initial polymer formation was too low to expect fire resistance.

After 50 laundry cycles, failures occurred with low-temperature drying for short periods of time. With 15.2% or 3.6% H_2O (150° F drying) or 7.9% H_2O (200° F drying), durability was reduced so that the samples failed the DOC test. However, increasing the mole ratio by about 50% did cause the samples with 3.6% or 7.9% H_2O (after drying) to pass the DOC after 50 washes. Yet, at the higher mole ratio there was only a slightly higher initial increase in polymer formation as measured by percentages of P and N. When H_2O was as high as 15.2%, the increased NH_3 again only slightly increased poly-

TABLE 3.—*Influence of the addition of air to* NH_3 *on the durability of the* THPOH-hot-NH_3 *finish*[1]

NH_3 flow (ft³/min)	Air flow (ft³/min)	Time of NH_3 exposure (s)	Phosphorus (%)	Nitrogen (%)	Results of VFT after No. of launderings	
					0	50
0.8	0	20	3.4	1.3	P	P
.8	.8	20	3.2	1.2	P	BL
.8	1.7	20	3.2	1.1	P	BL

P=passed. BL=borderline. VFT=vertical flame test (*9*). NH_3-to-THPOH mole ratio of 7:1.

[1] Lightweight sheeting padded with 40% THPOH, dried 45 s at 145° F. NH_3-to-THPOH mole ratio of 7:1.

TABLE 4.—*Effect of drying on the durability of* THPOH-hot-NH_3 *finish on flannelette*[1]

Dry temp. (°F)	Dry time (min)	H_2O (%)	Mole ratio 7:1				Mole ratio 11:1			
			Phosphorus (%)	Nitrogen (%)	DOC		Phosphorus (%)	Nitrogen (%)	DOC	
					Orig.	50 ×			Orig.	50 ×
150	0.5	15.2	4.2	2.0	P	F	4.5	2.3	P	F
150	1	3.6	4.1	1.6	P	F	4.3	2.1	P	P
150	2	2.6	4.1	1.6	BL	P	...	...	..	..
200	.5	7.9	4.0	1.8	P	BL	4.2	1.7	P	P
200	1	2.3	4.3	1.9	P	P	...	...	..	..
200	2	2.5	4.0	1.6	P	P	4.5*	2.1	P	P
260	.25	6.6	4.4	1.8	P	F	4.2	2.0	P	P
260	.5	2.3	3.7	1.8	BL	..	...	...	..	..
260	1	2.2	3.3	1.4	BL	..	3.2*	1.4	P	P
320	.25	5.9	4.3	2.0	P	P	4.5	2.3	P	P
320	.5	2.1	3.9	1.8	P	P	...	...	..	..
320	1	2.3	1.2	.6	F**	..	1.8*	0.7	F**	..

P=passed. F=failed. BL=borderline. DOC=Children's Sleepwear Standard (*4*).

* Mole ratio of 15:1.

** Assumed failures.

[1] Padded with 35% THPOH; 20-s exposure to hot NH_3.

mer formation, but it did not sufficiently improve the durability of the finish to pass the DOC after 50 cycles. Presumably this was due to surface polymer formation. It should be remembered, however, that at longer reaction times (5–10 min at room temperature) and higher mole ratios (50 or more to 1), a durable finish can be produced.

When the drying temperature was 320° F, even though H_2O was 2.3%, the initial polymer formation was too low to impart fire resistance. At 2.1%, the sample passed. Polymer formation was higher; drying time was 0.5 min. In this case, it is believed that loss of HCHO and possibly other volatile materials, prevented the polymerization. This loss in efficiency of the reaction can also occur when drying at low temperatures for a prolonged period of time, as reported by Berni et al. (*3*). The conclusion of this drying study is that drying temperatures can be varied over a wide range (150° to 320° F), but to produce a durable finish three conditions are necessary: (1) H_2O must be lower than 15% if the ammoniation time is to remain low (about 20 s); (2) an increase in mole ratio of NH_3 to THPOH can add a safety factor to impart the desired durability because, although apparently polymer formation is not increased, perhaps distribution is more favorable or molecular weight is higher, thus increasing the resistance of the polymer to being washed out of the fiber; and (3) a higher temperature can cause loss of monomeric materials and a reduced initial polymer formation.

Tubular Knit Treatment

In an initial study, a lightweight tubular knit fabric was processed continuously on the Benz range at a speed of about 0.75 yd/min which provides 2-1/2-min time in the drying oven and an equal time in the NH_3 reactor (80° C). The fabric was padded on the three-roll padder, then dried at 220° F, and ammoniated with a flow rate of 1.8 ft^3/min (9 mol/min). The initial P fixed in the fabric was 4.8% and N was 1.9%. After 50 laundry cycles, the sample had a char length of 2.0 inches (DOC test). A heavier knit fabric (8 oz/yd^2) was then treated for the Navy Clothing and Textile Research Unit, Natick Laboratories. Drying conditions, fabric speed, and ammoniation rates were adjusted to compensate for the heavier fabric. This material was processed continuously at about 1 yd/min. Drying was at 250° F, and was followed by ammoniation quench, oxidation, and wash. After 50 laundry cycles, the char length was 1.2 inches. It should be pointed out that the heavier knit was padded with a more dilute solution than the lightweight knit, thus the lower percentage of phosphorus. Data are shown in table 5.

Other Methods of Neutralization

Other methods of neutralization of THPC have been explored in the laboratory. Sodium sulfite (Na_2SO_3), disodium hydrogen phosphate dodecahydrate ($Na_2HPO_4 \cdot 12H_2O$), sodium citrate dihydrate ($Na_3C_6H_2O_7 \cdot 2H_2O$), sodium borate decahydrate ($Na_2B_4O_7 \cdot 10H_2O$), and sodium acetate ($NaC_2H_3O_2$) were used to neutralize aqueous THPC. Only the sulfite and the hydrogen phosphate were soluble enough to prepare THPOH solutions having 38% or more active solids. The other salts did not dissolve in concentrations greater than 34% THPOH.

Preliminary work with THPOH solutions prepared from sodium sulfite or disodium hydrogen phosphate in THPOH-NH_3 finishes on 4.0-oz flannelette has been encouraging. These solutions appear more stable than solutions neutralizd with sodium hydroxide and produce comparable finishes when evaluated under identical laboratory conditions using room-temperature NH_3. Pilot-plant evaluations with the new reac-

TABLE 5.—*Durability of* THPOH-hot-NH_3 *finish on tubular knit fabrics*

Tubular knit[1]	Dry temp. (°F)	Dry time (min)	NH_3 flow (mol/min)	Reaction time (min)	Phosphorus (%)	Nitrogen (%)	Char length (inches) after No. launderings[2]	
							0	50
Light	220	2½	9	2½	4.8	1.9	2.6	2.0
Heavy	240	2	18	2	3.8	1.9	1.0	1.2

[1] Lightweight knit padded with 40% THPOH, heavy with 35%.

[2] Children's Sleepwear Standard (*4*).

tor and hot NH_3 have been initiated. Results to date are incomplete.

SUMMARY AND CONCLUSIONS

A vertical ammonia reactor was constructed for the continuous production of fire-retardant materials. The ammoniation took place at about 75°–90° C. In general, with the hot NH_3, polymer formation became more efficient, distribution more even, and the process faster. At the higher temperature, the equilibrium reaction between NH_3 and H_2O to form NH_4OH is shifted to the left so that the amount of NH_4OH formed is negligible. It is believed that H_2O exists in the vapor form in the reactor and does not compete with the THPOH for the NH_3.

Although the theoretical mole ratio of NH_3 to THPOH is 1:1, under conditions described in this paper the lowest mole ratio for durability to 50 laundry cycles was found to be 3.5:1 to pass the VFT and about 6:1 to pass the DOC. Initial fire resistance can be imparted after as little as 5 s of ammoniation; however, reaction times of about 20–30 s were found necessary to produce durable finishes on lightweight goods.

THPOH-impregnated flannelette was dried over a range from 150° to 320° F to moisture contents of about 2% to 15% and ammoniated for 20 s. At each temperature, there were samples that passed the DOC after 50 laundry cycles.

Although the reaction between the THPOH and the NH_3 chemicals is virtually instantaneous, there appears to be a reaction delay caused by the rate of diffusion into the fibers. Obviously, heavier and tubular knit fabrics require a longer reaction time and a higher NH_3 flow. But even with the lightweight fabrics, there are lower limits to the ammonia flow, the reaction time, and the excess NH_3 needed to achieve the desired durability. Possibly this involves more complete polymerization within the fiber. Just as the NH_3 continued to react with the THPOH-impregnated sample when being held in the polyethylene bags, even in the "inaccessible" areas under the embroidery hoops, it may be that additional reaction time is needed for the formation of the polymer in a more favorable manner within the fiber to attain the desired durability.

ACKNOWLEDGMENTS

We are indebted to the following Southern Regional Research Center personnel: Bill Latour and Laurey Richard for assistance in the construction and development of the NH_3 reactor; Esmond Keating for engineering; Biagio Piccolo for phosphorus analyses; and John Mason and Ann Black for nitrogen analyses. Laundering was done by Lionel Williams and was tested by Judy Bogatz and Raymond Richard. Our assistants in the pilot-plant processing were Milton Hoffman, James Franklin, and Woody Carter.

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STRENGTH OF INDIVIDUAL FIBERS TREATED WITH THE FLAME RETARDANT THPOH-NH_3

By Louis C. Weiss, Frederick R. Andrews, and Charles B. Hassenboehler[1]

(Presented by Louis C. Weiss)

INTRODUCTION

Flame-retardant textiles are a technological advance which can protect thousands of us from a terrible loss. Recent action by Congress emphasizes and expands the need for marketable flame-retardant fabrics. The Southern Regional Research Center has produced effective flame-retardant treatments, some of which are now acceptable for cotton markets. To be commercially acceptable, the treatment of the fiber must not only be durable and inexpensive, but also must have no adverse effects upon the physical properties of the fabric.[2] To assess these qualities, certain questions should be answered: Are the physical structure and strength of the fiber altered? Is the chemical merely deposited on the surfaces of the fiber and yarn, or are these surfaces bonded together by the chemical reaction? As with many textile improvements that become commercially important, an investigation of the individual fiber is needed.

MATERIALS AND METHODS

Alterations in the physical properties of cotton caused by the flame-retardant treatment tetrakis (hydroxymethyl) phosphonium hydroxide with an ammonia vapor cure (THPOH-NH_3)[3] were investigated. The experimental design is outlined in table 1. Only 100% cotton fabric was used from a genetically homogeneous variety of American Upland cotton, *Gossypium hirsutum* 'Deltapine 15', and all fabrics were first desized and scoured. The fibers and fabrics were treated at the same time and, where possible, the same change in parameter was made during treatment of the fiber that was made during treatment of the fabric. Fabric strips were broken according to standards of the American Society for Testing and Materials. Fibers were evaluated at a gage length of 7.2 mm on a special electronic tensile tester. Details on these techniques have been published.[4]

TABLE 1.—*Samples*

Controls: Scoured cottons

THPOH-NH_3:
- A. Printcloth:
  - 1. Fabrics:
    - 2 constructions
    - 2 pretreatments
  - 2. Parameters:
    - 4 concentrations
    - 3 moisture conditions
    - 3 tensions during treatment
- B. Other fabrics:
  - Sheeting
  - Basketweave
  - Sateen
- C. Single fibers from kiered roving

RESULTS

This is the first time properties of individual, flame-retardant, cotton fibers are presented. Their strength was related to regain of fiber moisture, with modulus and strain changing less than breaking load. Fiber strain recovery increased slightly. This was characterized by defining the increased or differential strain recovery as the recovery of the treated fiber minus the recovery of the control, then dividing the remainder by the recovery of the control and multiplying by 100 for percentages:

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$$\frac{\text{Treated—control}}{\text{Control}} \times 100.$$

All fiber samples were measured after relaxing from a 2% strain. Typical results are presented in figure 1. The amount of chemical reaction is indicated. For THPOH-NH_3 "% P" is the percentage of combined phosphorus. For dimethylol ethyleneurea (DMEU), "x/hagu" is the calculated cross-links per hundred anhydroglucose units.

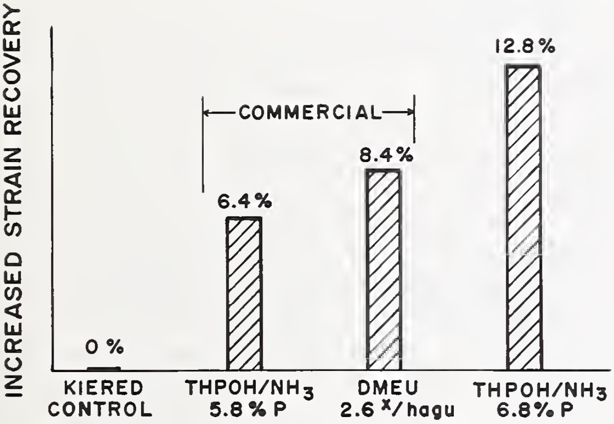

FIGURE 1.—Mean recovery of individual cotton fibers after relaxing from a 2% strain.

All treatments showed strain recovery of the modified fibers greater than their control. In the range of commercial treatments, fibers modified by THPOH-NH_3 had less recovery than those modified by the durable-press treatment, DMEU.[5] Yet, as the bar on the right shows, increasing the THPOH-NH_3 treatment did increase the strain recovery.

For flame-retardant cotton, fiber modulus was linearly related to fabric modulus. Whereas single fibers lost 25% of their strength, comparable fabrics lost only 10%. Concurrently, comparisons of the fabric thread counts with increases in weight per square yard and in fabric thickness suggest that this flame-retardant treatment deposited a relatively large amount of material on the surfaces of the fibers and yarns. The retained strength of fabrics was apparently aided by the bonding action of this copolymer complex. Awareness of this should assist industry in commercializing flame-retardant cotton.

Shear and bending properties of flame retardant cottons comprising many variations in fabric structure and treating conditions were also measured in order to characterize an esthetic textile quality called "handle" or hand. This is important in marketing chemically modified textiles. Shearing strain provided an inverse index of fabric stiffness that relates to hand—the higher the strain, the lower the shearing stiffness and perhaps the more suitable the hand. A 3-by-3 basket weave, instead of a special plain weave, possessed the softer hand for these treated fabrics.

ACKNOWLEDGMENTS

Thanks are expressed to George L. Drake, Jr., of the Southern Regional Research Center, for guidance in the THPOH-NH_3 treatment, and to Thomas J. Taggart, formerly of the Center, for assistance with the special fabric test.

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[5] See footnote 4.

OXYLUMINESCENT BEHAVIOR OF FLAME-RETARDANT COTTONS

By Robert A. Pittman, Dorothy C. Heinzelman, and Verne W. Tripp[1]

(Presented by Robert A. Pittman)

Oxyluminescence is the emission of (visible) light by a material when heated in the presence of oxygen. This is a report of preliminary work done to investigate the feasibility of using the observation of oxyluminescent behavior of cellulose products as a technique in evaluating flame retardants applied to cotton textile products and to elucidate the mechanisms associated with the oxidation of these products.

A heater driven by a linear temperature programer and a microphotometer to measure the light emitted were used. The sample, mounted on the heater, and the photomultiplier tube were enclosed in a lightproof box. A slow stream of air was allowed to pass through the sample chamber. The data were recorded on an X-Y recorder; the X-axis recorded the temperature as measured by a thermocouple and the Y-axis recorded the light intensity. Data were taken over the temperature range 50° to 200° C. The rate of heating was approximately 10° to 15° C per minute.

The fact that cotton cellulose exhibited oxyluminescence was first observed by workers at the Southern Regional Research Center in 1962.[2] A variety of chemically modified cotton textiles was examined by the technique described. Some of the results of this study are given in table 1. This earlier work showed the feasibility of studying the oxidation of modified cottons at preignition temperatures by means of oxyluminescence. Plots constructed of ln I versus $1/T$, where I is light intensity and T the absolute temperature, were used to determine the apparent activation energy of the reaction.

In the present study, cotton fabrics given four different flame-retardant treatments were examined. They were—

1. THPC-urea-Na_2HPO_4 flannel (percent add-on: 0, 17, 19, 24).
2. THPC-amide sateen (percent add-on: 0, 9, 15, 19).
3. THPOH-NH_3 printcloth (percent add-on: 0, 12, 17, 22).
4. THPC-trimethylolmelamine (TMM) sateen (percent add-on: 0, 7, 10, 14, 18, 23, 27).

Nearly all samples (except 22% THPOH-NH_3) of treated cloth emitted less light than the untreated control fabrics. This indicates a lower rate of oxidation for the treated samples, as one

TABLE 1.—*Oxyluminescence of untreated and chemically modified cotton fabrics*

Sample No.	Description or derivative	Light intensity[1] at 200° C
1	80×80 printcloth scoured and bleached	46
2	80×80 gray cloth (control for sample 1)	111
3	Sample 2 bleached in NaClO for 10 min and rinsed in H_2O	52
4	Phosphonomethylated	101
5	Formaldehyde treated W	32
6	Formaldehyde treated D	41
7	Phosphorylated	0
8	APO	241
9	Aminized	502
10	Mercerized	35
11	Partially acetylated (25% acetyl)	26

[1] Arbitrary units.

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[2] Pittman, Robert A., and Tripp, Verne W. 1962. Oxyluminescence from cotton textiles. Text. Res. J. 32: 1038–1040.

might expect. Plots of ln I versus $1/T$ gave approximately straight lines. Best-fit straight lines for the data were calculated, and the slopes and intercepts obtained were used to calculate the frequency factors and apparent activation energies (table 2).

These results can be interpreted as the energy barrier which must be overcome for the reaction to take place (activation energy) and as an indication of change in entropy accompanying the reaction (frequency factor). The THP-TMM system seems to differ from the control in terms of change in these parameters more than the other three systems studied. The reason for this difference is not presently known. These data indicate the potential of oxyluminescence as a tool for studying reaction kinetics of oxidation at low temperatures in flame-retardant cellulose composites.

TABLE 2.—*Frequency factors* (A) *and activation energies* (E_a) *for some flame-retardant treatments*

Sample	Add-on (%)	Log A	E_a (kcal/mole)
THPOH-NH_3 (printcloth).	0	9.40	14.30
	12	8.68	13.53
	17	9.46	15.03
	22	9.64	14.47
THPC-amide (sateen).	0	9.33	13.28
	9	8.68	13.04
	15	8.46	12.27
	19	8.12	11.47
THPC-urea-Na_2HPO_4 (flannel).	0	10.72	16.38
	17	9.68	15.32
	17	8.25	12.36
	19	8.94	14.00
	24	10.59	17.01
THPC-TMM (sateen).	0	9.12	12.98
	7	7.90	10.82
	10	5.94	6.97
	14	6.34	7.81
	18	6.29	7.64
	23	6.08	7.36
	27	6.08	7.45

Table 3 presents data correlating the observed oxyluminescence and the limiting oxygen index widely used as a measure of flame resistance. The decrease in light emission with increasing oxygen index is evident from these data and suggests the potential use of oxyluminescence as a method of evaluating flame retardancy.

It was also of interest, of course, to examine the behavior of polyester/cotton blends. Although data from some series of such blends gave erratic results, improved instrumental design could apparently obtain information on oxyluminescence of such materials successfully. Table 4 gives the data for these specimens.

TABLE 3.—*Intensity of light emission at 200° C versus oxygen index for cotton treated with* THPC-TMM

Add-on (%)	Light intensity[1]	Oxygen index
Control	1,245	0.19
7	999	.24
10	921	.26
14	696	.28
18	761	.31
23	635	.36
27	581	.41

[1] Arbitrary units.

TABLE 4.—*Oxyluminescence of polyester/cotton blend fabrics*

Cotton (%)	Light intensity[1] at 200° C
50	46
67	55
77	54
89	60
100	80

[1] Arbitrary units.

MEETING THE MATTRESS FLAMMABILITY STANDARD WITH TREATED COTTON BATTING[1]

By J. P. Neumeyer,[2] P. A. Koenig,[3] and N. B. Knoepfler[2]

(Presented by J. P. Neumeyer)

ABSTRACT

The general provisions of DOC FF 4-17, "Flammability Standard for Mattresses," and the technical problems that it presents to the cotton innerspring mattress industry are briefly described. Thermogravimetric data indicated that well-known flame retardants containing phosphorus decompose when exposed to the high temperatures that exist inside a smoldering mattress and are thus ineffective in preventing the smoldering combustion process. Treatment with inorganic compounds that contain boric oxide (B_2O_3) prevented cigarette-induced smoldering combustion in mattresses. Common to these compounds is the formation of glassy films upon heating. The B_2O_3 glass is stable to temperatures higher than that attained under normal smoldering conditions. The B_2O_3 donor compounds, their respective treating formulations, and the effect of the treatments on the physical properties of cotton batting are discussed. The results of exposure to elevated temperature and humidity for extended periods of time are presented.

INTRODUCTION

The "Flammability Standard for Mattresses," DOC FF 4-72 is scheduled to become effective June 7, 1973. There are, however, indications that a 6-month delay may be allowed (*2*, *8*).[4] All mattresses, as defined in the standard, manufactured for sale on or after the effective date shall comply with the standard. Mattresses which are in inventory or with the trade on the effective date shall be exempt from the standard.

The test method involves measuring the ignition resistance of the mattress surface by exposure to lighted cigarettes in a draft-protected environment. These exposures include smooth, tape edge, and quilted or tufted areas on the mattress surface. Two-sheet tests are also conducted on similar surface locations. In the latter test, the burning cigarette is placed between the two sheets. At least 18 cigarettes must be burned on the test surface, 9 in the bare-mattress tests and 9 in the two-sheet tests. A test location passes the test if the char length on the mattress surface is not more than 2 inches in any direction from the nearest point of the cigarette.

DOC FF 4–72 places a considerable burden on the cotton mattress manufacturer. When subjected to the slow and continuous cigarette heat source, the insulative property of cotton filling materials is significant in the initiation and sustainment of smoldering combustion. The energy generated by the cigarette is accumulated directly beneath it. As the local temperature increases, the filling material generates additional energy by exothermic combustion. A further increase in temperature results. Conditions are finally such that the smoldering combustion process sustains itself even after the source of ignition is removed.

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[1] This work is being carried out under a cooperative agreement with the National Cotton Batting Institute and under a memorandum of understanding with the Textile Fibers and ByProducts Association and the National Cottonseed Products Association.

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[4] Italic numbers in parentheses refer to items in "Literature Cited" at the end of this paper.

The standard requires only that a mattress be resistant to ignition by a cigarette. No provision is made for open-flame testing. This is rather disconcerting when one considers that bedding fires initiated by open flames (match or methanimine pill) develop more rapidly and reach hazardous levels sooner than those initiated by a smoldering cigarette (*1*). The omission of an open-flame test allows highly flammable polyurethane foam to pass the standard.

RESULTS AND DISCUSSION

One method of making a cotton mattress comply with the standard is to treat the filling material with an appropriate compound, rendering it smolder resistant. To this end a number of phosphorus and boron formulations were evaluated by immersing and padding cotton raw stock to 100% wet pickup. The raw stock was dried and garnetted into batts consisting of 20 webs. The batts were used as filling materials in constructing minimattresses (*7*), which were in turn tested for ignition along the tape edge by (1) a single cigarette on the bare surface of the mattress, (2) a single cigarette positioned between two sheets on the mattress surface, and (3) two cigarettes side by side on the bare surface. The two-cigarette test is the most severe and the single cigarette on the bare surface is the least severe test.

Table 1 summarizes the results obtained by evaluating phosphoric acid, urea phosphate, THPC-amide, and borax:boric acid treatments. In each of the phosphorus systems the total add-on was unfeasibly high and excessive acid degradation of the filling material was apparent. Whereas phosphorus compounds are considered to be among the most efficient flame retardants currently available for cotton fibers and fabrics, it is obvious from table 1 that they are not at all efficient for preventing smoldering combustion of cotton filling materials installed in a mattress. This is directly attributable to the different mechanisms by which flaming and smoldering combustion proceed and to the heat transfer environment unique to mattresses.

TABLE 1.—*Add-on required to pass cigarette ignition test of minimattresses*

Treatment	Add-on (%)	
	1 cigarette, bare mattress—tape edge	2 cigarettes, bare mattress—tape edge
Phosphoric acid	21.4	39.9
Urea phosphate	29.5	>36.3
THPC-amide	31.8	>54.0
Borax:boric acid, 7:3	8.5	20.0

The smoldering process, by definition, is the burning and smoking or wasting away by a slow and suppressed combustion without flame. For the most part, the energy evolved is a direct result of the exothermic oxidation of the solid char products remaining from the pyrolytic degradation of the material. Flaming combustion, on the other hand, is that phenomenon observed when the gaseous pyrolysis products are oxidized at such a rapid rate as to produce heat and light. Phosphorus compounds interfere with the course of pyrolysis to direct the formation of increased amounts of combustible char and reduced amounts of flammable gases. This results in less gaseous fuel for the flaming process by creating more solid fuel for the smoldering process.

Cotton batting with as little as 8.5% total add-on of a 7:3 borax:boric acid mixture passed the single-cigarette test. Only 20.0% was required to pass the more severe two-cigarette test. These results demonstrate a significant improvement in performance over the phosphorus compounds. One of the important mechanisms of fire retardance with borates is thought to be the formation of glassy films (*5*). For example, on heating boric acid (H_3BO_3) one mole of water is lost between 130° and 200° C to form metaboric acid (HBO_2). Additional heating results in the loss of more water to form boric oxide (B_2O_3). The boric oxide glass softens at 325° C and flows freely at about 500° C. This melt is stable to temperatures in excess of 750° C and thus provides an effective coating of the fibers during most of the combustion process (*4*). (See fig. 1.)

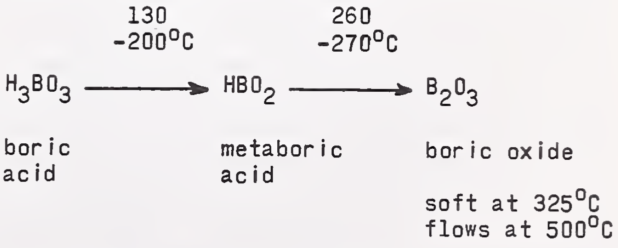

FIGURE 1.—The formation of boric oxide by heating boric acid.

Table 2 shows the results obtained from a series of tests in which the ratio of borax to boric acid was varied at the 15% add-on level. The data strongly indicate that boric acid is the necessary component in preventing the smoldering process. Borax is a sodium borate containing 0.45 parts of sodium oxide (Na_2O) to 1.0 part of B_2O_3. Its poor performance is thought to be a result of a catalytic effect that its sodium ions have on the char oxidation. Walker (*9*) cited the alkali metals as having a catalytic effect on the oxidation of carbon.

TABLE 2.—*Cigarette test on tape edge of mini-mattresses*

[Borax:boric acid mixtures on batting at 15% add-on]

Borax: boric acid ratio	1 cigarette		2 cigarettes, bare mattress
	Bare mattress	Between 2 sheets	
0:1	N	N	N
6:5	N	N	I
7:3	N	N	I
1:0	I	I	I

N=No ignition.
I=Ignition.

In order to further investigate the apparent difference between the phosphorus and boron systems, 1/8-inch felts of purified cellulosic linters were impregnated with reagent grade samples of boric acid, borax, and diamonium phosphate, and were evaluated by thermogravimetric analysis (*4*). A DuPont 951 thermogravimetric analyzer was used at a heating rate of 5° C/min over a temperature range from ambient to 750° C. An 8.4% oxygen/91.6% nitrogen atmosphere at a flow rate of 85 ml/min continuously purged the system. The heating rate and the oxygen concentration were chosen to allow controlled monitoring of the weight loss reactions.

Figure 2 shows the weight loss curve (TG) and the rate of weight loss curve (DTG) for untreated cellulosic linters. The major weight loss occurs between 280° and 380° C and is referred to as a thermal decomposition or pyrolysis, to yield flammable volatiles and carbonaceous char. The carbonaceous char residue undergoes combustion between 450° and 580° C. The rate of weight loss associated with the char combustion is much slower than the rate of the pyrolytic decomposition reaction.

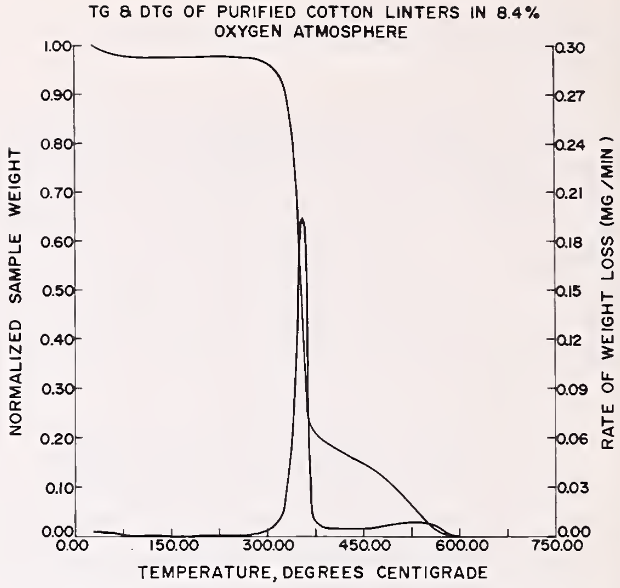

FIGURE 2.—Thermogravimetric data for purified cotton linters in an oxygen atmosphere.

The DTG data for boric acid, borax, and diammonium phosphate are shown in figure 3. Borax loses essentially all of its water of hydration between 50° and 150° C. Thereafter it is present as the stable anhydrous sodium borate ($Na_2O \cdot 2B_2O_3$). Boric acid loses essentially all of its water and is present as boric oxide by 200° C. The decomposition of diammonium phosphate is apparently much more complex. Based on weight loss data, the first two peaks correspond to the loss of 2 moles of ammonia with subsequent formation of phosphoric acid. The phosphoric acid is dehydrated between 300° and 500° C to form polyphosphoric acid (HPO_3), which is a glassy polymer (*6*). Rapid weight loss is centered about 600° C. The glassy polyphosphoric acid apparently decomposes between 500° and 700° C since only about 20% residue remains at 700° C.

Figure 4 shows the DTG curves for linters containing approximately 5% and 15% diammonium phosphate salt. As the concentration is increased, the onset temperature of weight loss decreases. Untreated cellulose begins to show a weight loss (other than free water) at about 220° C, whereas samples treated with 5% and 15% diammonium phosphate begin to lose weight at 155° and 135° C, respectively. Two peaks are observed above 450° C, both of which can be associated with the combustion of the carbonaceous char. If the weight loss of diam-

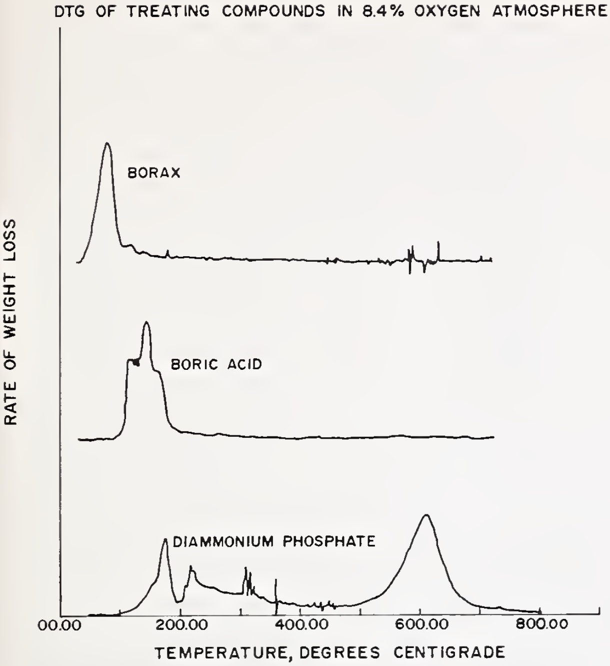

FIGURE 3.—DTG curves for pure borax, boric acid, and diammonium phosphate.

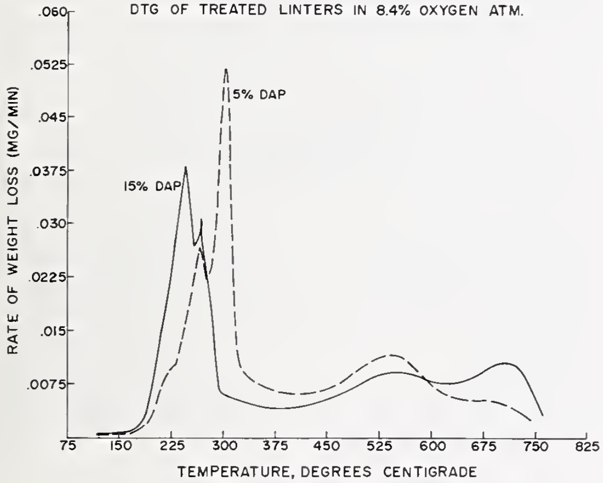

FIGURE 4.—DTG data for purified linters treated with 5% and 15% add-on of diammonium phosphate.

monium phosphate centered about 600° C (fig. 2) is indeed a decomposition of the HPO_3 coating. then one might expect that any retardation of the solid-state char combustion would diminish with a subsequent increase in the rate of weight loss of the combusting char. The rate of char weight loss would then most definitely appear as two distinct peaks as shown in figure 5.

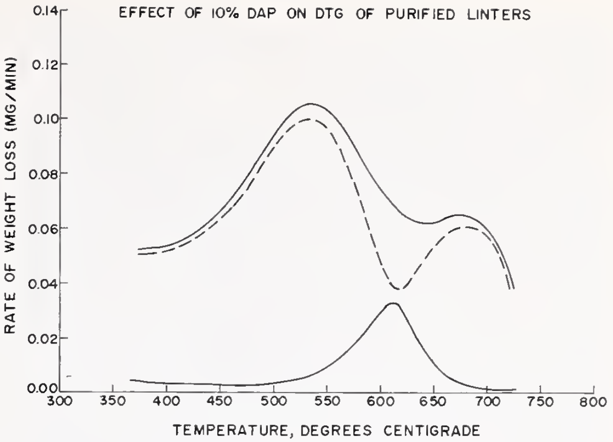

FIGURE 5.—Effect of diammonium phosphate on DTG data of purified linters between 400° and 725° C.

This figure shows the DTG curves for pure diammonium phosphate, linters treated to a 10% add-on of diammonium phosphate, and a curve representing the difference between the two. The difference curve is a reflection of the weight loss attributed to the cellulose combustion alone. The rate of weight loss diminishes from 525° to 620° C and then suddenly increases after the polyphosphoric acid glassy film volatilizes. From figure 4, it is apparent that the increase in rate of weight loss, after the polyacid coating volatilizes, is directly proportional to the original concentration of diammonium phosphate.

In summary, cellulose treated with diammonium phosphate would be protected at temperatures below 500° C, but at temperatures above 500° C, as often occurs locally in a smoldering mattress, this protection would be lost when the glassy polyacid decomposes.

The effect of borax on both the pyrolytic and char oxidation reactions is shown in figure 6. Note that the thermal stability of borax-treated cellulose is about the same as untreated cellulose. Unlike diammonium phosphate, an increase in the borax concentration does not shift either the onset temperature at which weight loss begins, or the temperature of maximum rate of weight loss. The maximum rate of pyrolytic weight loss, however, does decrease with increased add-on, suggesting improved flame retardance. The weight loss associated with the char oxidation is more complex than the char oxidation of untreated cellulose. The maximum rate of weight loss occurs at 536° C for untreated cellulose, whereas the maximum for the 5% borax treatment was lowered by 51° C to 485° C. There appear to be three peaks of weight loss associated with the char oxidation.

The inhibiting effect of boric acid on smoldering combustion can be explained by thermogravimetric analysis. Figure 7 shows the DTG data for cellulosic linters treated with boric acid. Unlike Lewis acids, which lower thermal stability, boric acid increases stability with increasing add-on. Although boric acid is a weak acid, at the pyrolysis temperature of cellulose it is not in its acid form, having dehydrated to the oxide. Increasing the thermal stability delays the onset of exothermic activity associated with the oxidation of the volatile pyrolysis products. The rate of char oxidation is reduced considerably. A 5% add-on reduced the maximum rate by 16%; 15% add-on reduced the rate by 30%.

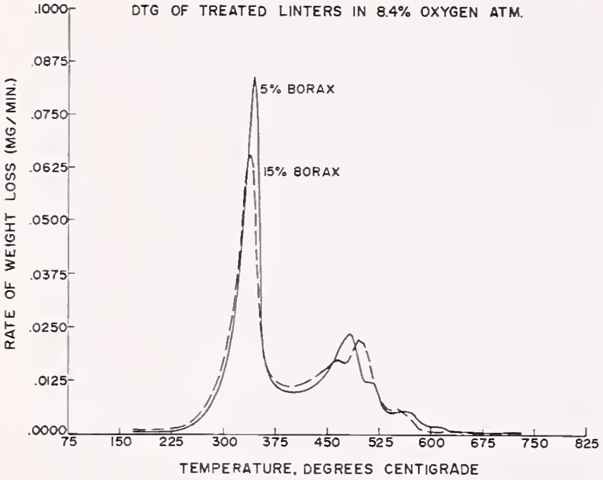

FIGURE 6.—DTA curves of linters treated with 5% and 15% add-on of borax.

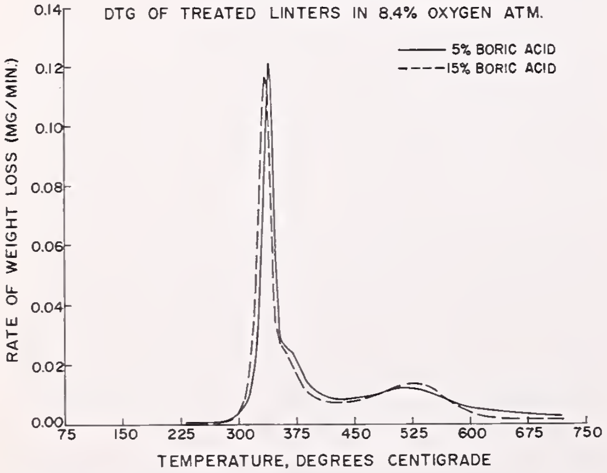

FIGURE 7.—DTG curves of linters treated with 5% and 15% add-on of boric acid.

Table 3 summarizes the thermogravimetric data. The rate data were normalized by dividing the weight loss for the specific reaction into the maximum rate of that reaction. In the case of diammonium phosphate, which lost weight concurrently with the cellulose, that portion of the weight loss and rate attributed to the decomposition of the additive were subtracted before the rate of cellulose weight loss was normalized. Notice that diammonium phosphate lowers the thermal stability of the cellulose as the add-on increases. Diammonium phosphate also appreciably decreases the rate of the weight loss associated with the oxidative pyrolysis reaction. Borax and boric acid do not noticeably affect the thermal stability. Note, however, that borax does decrease the rate of volatilization with increasing add-on.

Table 3 also lists maximum rates of char oxidation. Borax, a very poor suppressor of afterglow, does not slow down the rate of oxidation. The temperature of maximum weight loss is about 60° C below that observed for the untreated cellulose control, suggesting some catalytic activity. With diammonium phosphate the maximum rate of reaction for the initial oxidation of the char is between 30% and 40% less than the control. However, in what has been termed a secondary oxidation of the char, occurring at over 650° C, the maximum rate of combustion is over twice that of the control. Boric acid demonstrates reductions in reaction rate similar to diammonium phosphate in the 500°–600° C temperature range. However, unlike diammonium phosphate, boric acid does not exhibit any secondary oxidation of the char.

The apparently superior high-temperature protection of boric acid over borax and diammonium phosphate is further evidenced by cellulosic residues remaining at 725° C. After compensating for the amount of flame-retardant residue, the percentage of cellulosic residue was calculated. The results for the 5% and 15% add-ons are shown in table 4. It is quite evident that boric acid inhibits high-temperature char oxidation to a much greater extent than either borax or diammonium phosphate.

The vapor pressure of boric acid is relatively high (*3*). Under adverse conditions, particularly high temperature and elevated humidity, boric

TABLE 3.—*Thermogravimetric data*

Compound	Normalized maximum rate					
	Oxidative pyrolysis		Oxidation of char		Secondary oxidation of char	
	Temp. (°C)	Rate (mg/min/mg)	Temp. (°C)	Rate (mg/min/mg)	Temp. (°C)	Rate (mg/min/mg)
Control	357	0.253	536	0.050	...	...
5% DAP	305	.097	540	.034	670	0.060
10% DAP	280	.087	535	.035	675	.105
15% DAP	245	.087	545	.032	715	.06
5% borax	343	.165	485	.050	...	...
10% borax	343	.125	475	.050	...	...
15% borax	337	.110	495	.056	...	...
5% boric acid	335	.175	525	.042	...	...
10% boric acid	340	.184	525	.035	...	...
15% boric acid	340	.191	520	.036	...	...

acid will be lost through volatilization. A series of experiments were designed to evaluate ammonium pentaborate and sodium borate as boric oxide donors by determining (1) the add-on required for smolder resistance and (2) their durability to elevated temperatures and humidity. Ammonium pentaborate was at add-on levels of 5%, 7.5%, 10%, and 15%. The results, shown in table 5, indicate that an add-on of about 10% by weight would be sufficient to pass the DOC FF 4–72 standard.

A sodium borate (0.25 Na_2O/B_2O_3) was evaluated at 5%, 10%, and 15% add-on levels. This ratio of sodium oxide to boric oxide provides very good solubility in water. Cigarette tests results are shown in table 6. Again, 10% appears adequate for passing the DOC FF 4–72 standard. Poor results were obtained with borax (table 2), which is a sodium borate with 0.45 Na_2O/B_2O_3. As alluded to earlier, the presence of excessive amounts of sodium ions is thought to catalyze the char oxidation to an extent which surpasses the inhibiting effect of boric oxide.

Table 7 shows the results of cigarette testing of minimattresses containing 10% add-on of boric acid, borax: boric acid in a 1:1 ratio, and a 5:1 mixture of boric acid: ammonium carbonate. The ammonium carbonate increases the solubility of boric acid in water by forming the more soluble ammonium borates.

Samples of all the treatments shown in tables 5, 6, and 7 were observed when exposed to an open flame. Only those with sodium oxide present demonstrated a significant resistance to flaming combustion. These observations were

TABLE 4.—*Percentage of residue at 725° C*

Compound	5% add-on	15% add-on
Boric acid	4.4	10.0
Borax	1.0	.0
Diammonium phosphate	.1	.1

TABLE 5.—*Cigarette test on tape edge of minimattresses, batting treated with ammonium pentaborate*

Add-on (%)	1 cigarette		2 cigarettes, bare mattress
	Bare mattress	Between 2 sheets	
5.0	N	N	I
7.5	N	N	I
10.0	N	N	N
15.0	N	N	N

N = No ignition.
I = Ignition.

TABLE 6.—*Cigarette test on tape edge of minimattresses, batting treated with sodium borate*[1]

Add-on (%)	1 cigarette		2 cigarettes, bare mattress
	Bare mattress	Between 2 sheets	
5.0	N	I	..
10.0	N	N	N
15.0	N	N	N

N = No ignition.
I = Ignition.
[1] 0.25 Na_2O/B_2O_3.

predicted with the thermoanalytical results shown in figures 6 and 7 and table 3.

All of the samples were analyzed for boric oxide content. The results of the analyses and of cigarette ignition tests are compiled in table 8. Note that in all of the tests sufficient boric oxide was present to inhibit ignition of the bare minimattress by a single cigarette. When the boric oxide content exceeded 4.11% the samples consistently passed the two-sheet test. With a boric oxide content of 5.81% or greater, the minimattresses exhibited a factor of safety by passing a test in which two lighted cigarettes were placed side by side on the bare surface.

Table 7.—*Cigarette test on taped edge of minimattresses, batting treated with borax:boric acid, 10% add-on*

Borax: boric acid ratio	1 cigarette		2 cigarettes, bare mattress
	Bare mattress	Between 2 sheets	
0:10	N	N	I
[1]10:10	N	N	N
5:5	N	N	I

N=No ignition.
I=Ignition.
[1] 2% ammonium carbonate added to improve solubility.

Table 8.—*Add-on required to pass cigarette ignition test of minimattresses*

B_2O_3 content (%)	1 cigarette on tape edge		2 cigarettes on tape edge
	Bare mattress	2 sheets	
2.51	N	N	I
3.03	N	N	I
3.23	N	N	I
3.35	N	I	. .
3.39	N	N	I
3.48	N	N	I
3.63	N	N	I
3.87	N	N	N
4.00	N	I	. .
4.11	N	N	N
4.43	N	N	I
4.68	N	N	N
4.73	N	N	N
4.82	N	N	I
5.09	N	N	I
5.36	N	N	N
5.63	N	N	I
5.81	N	N	N
8.48	N	N	N
8.84	N	N	N

N=No ignition.
I=Ignition.

To evaluate the durability of these samples to temperature and humidity, they were maintained at temperatures of 70°, 105°, 130°, and 160° F with relative humidity of 65% for up to 35 days. Approximately every 7 days the samples were analyzed for boric oxide content. All samples experienced decreasing boric oxide content with exposure time. The losses were greater at higher temperatures.

Figures 8, 9, 10, and 11 demonstrate this phenomenon. The boric oxide concentrations were normalized in all cases and the best linear, least aqueous fit to the data are shown for each temperature. Only data at the beginning and the end of the test period were obtained at 160° F; therefore, a straight line was assumed. It is more likely, however, that a steady-state concentration close to the final concentration was reached before the end of the exposure time. The data are incomplete to allow the prediction of durability of the treatments over longer periods of time at the other three temperatures.

Figures 12 and 13 show comparative temperature/humidity stability curves at 70° and 105° F for four different boric oxide donors. The sodium borate compound is the most stable of the four, followed by the boric acid with ammonium carbonate added, then the ammonium pentaborate, and finally the boric acid alone. The increased stability of the boric acid with ammonium carbonate mixture is attributed to the formation of ammonium biborate.

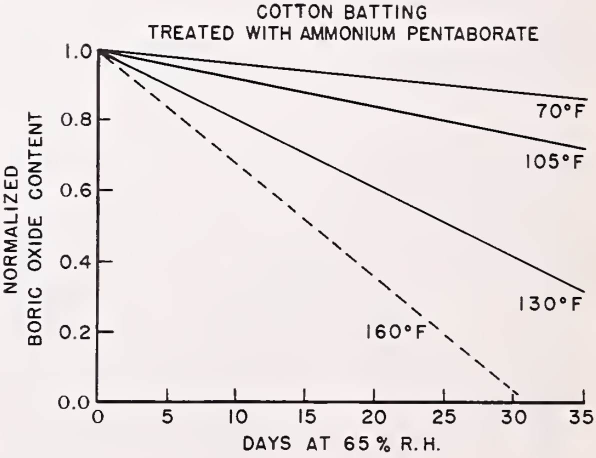

Figure 8.—Durability of ammonium pentaborate treatment to elevated temperatures at 65% relative humidity.

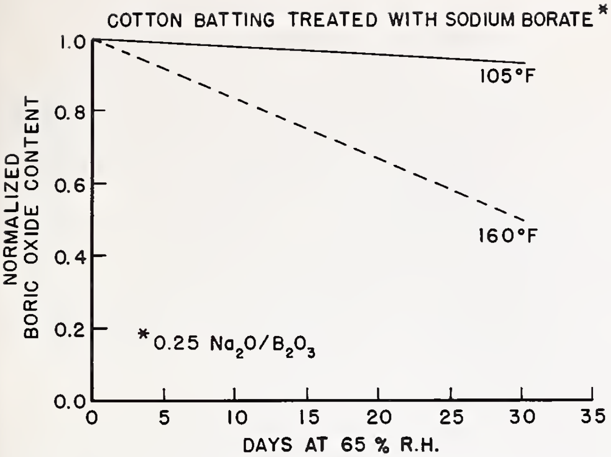

FIGURE 9.—Durability of sodium borate treatment to elevated temperatures at 65% relative humidity.

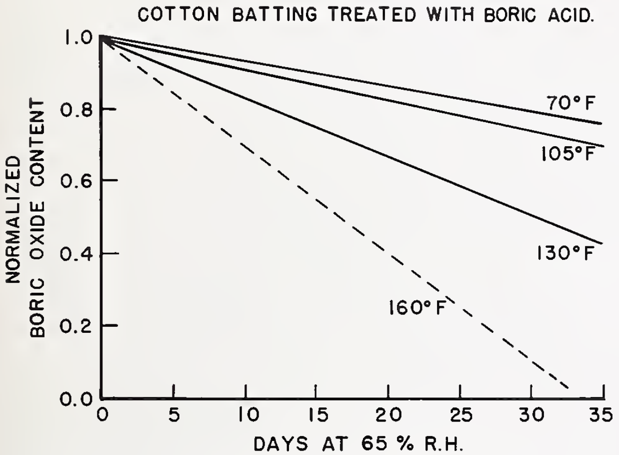

FIGURE 10.—Durability of boric acid treatment to elevated temperatures at 65% relative humidity.

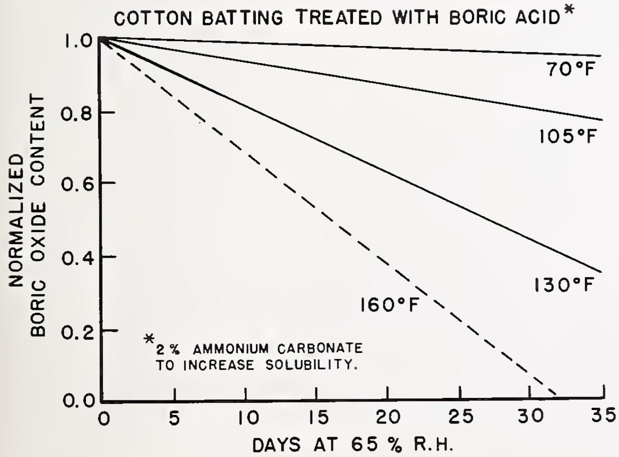

FIGURE 11.—Durability of boric acid-ammonium carbonate treatment to elevated temperatures and 65% relative humidity.

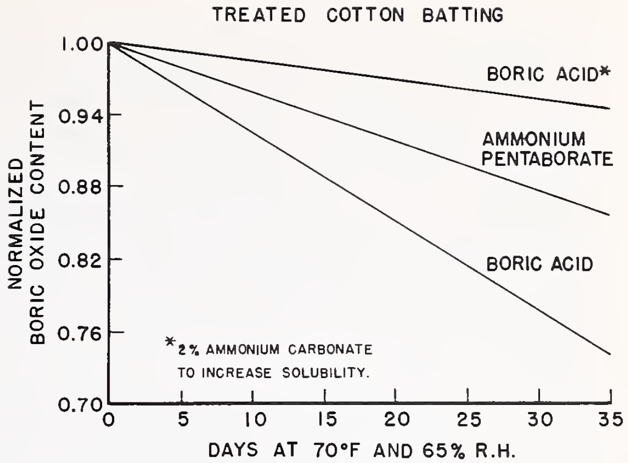

FIGURE 12.—Durability of treatment to 70° F and 65% relative humidity.

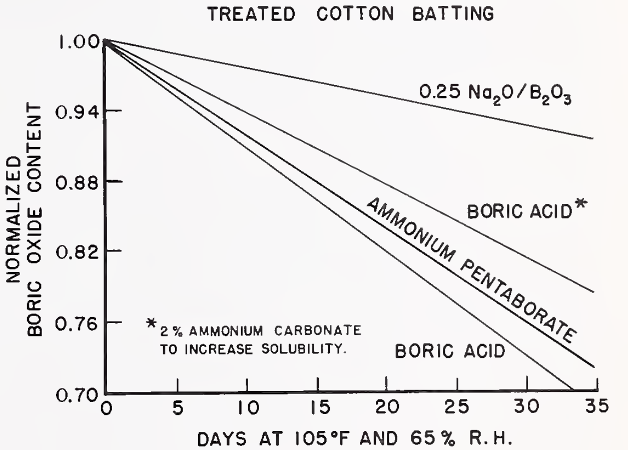

FIGURE 13.—Durability of treatment to 105° F and 65% relative humidity.

SUMMARY

Research has indicated that the classical approach to cellulose flame retardance by a Lewis acid mechanism is not well suited for preventing smoldering combustion in cellulosic filling materials. Although such treatments decrease the rate of combustion, they also provide more fuel for the smoldering reaction.

Boric oxide systems have proved to be effective in preventing smoldering combustion. Upon heating, these systems form stable coatings that help inhibit heat and mass transfer to the fibers. Thus, the combustion reaction rates are significantly decreased without corresponding large decreases in pyrolysis temperature.

Boric acid and ammonium pentaborate at the 10% add-on level provide sufficient boric oxide content to pass both the bare mattress and two-sheet single-cigarette tests in the minimattress configuration. Sodium borate systems can be as effective as long as the sodium oxide content is not in excess. For example, 15% add-on of sodium borate (0.25 Na_2O/B_2O_3) passed the two-cigarette tests, whereas a sodium borate (0.45 Na_2O/B_2O_3) at 15% add-on failed the single-cigarette test.

Several boric oxide systems were evaluated for durability to exposure of 35 days at 65% relative humidity and temperatures of 70°, 105°, and 160° F. The sodium borate treatment is the most stable, followed by the boric acid with ammonium carbonate added, then the ammonium pentaborate, and finally the boric acid alone. The addition of ammonium carbonate increases the solubility of boric acid in water.

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ELECTRON MICROSCOPY OF FLAME-RESISTANT FABRICS

By Wilton R. Goynes, Eileen K. Boylston, Linda L. Muller, and Brenda J. Trask[1]

(Presented by Wilton R. Goynes)

In the development of flame-retardant cotton fabrics, microscopy can be used to determine the mechanisms by which the retardant agent functions, and how effectively the fabric has been treated with the agent. Though effectiveness of flame retardants can be measured by flame, laundry, and weathering tests, such testing contributes little to the understanding of why or how a sample passed or failed. In this study, light and electron microscopy were used on cotton fabrics treated with flame-retardant agents, largely those based on tetrakis (hydroxymethyl)-phosphonium chloride (THPC).

Dyeing treated fabrics with dyes specific for a chemical finish is a relatively quick method of determining the degree of penetration of the finish. The stained fabrics, or fiber cross sections, are examined with the light microscope for uniformity of penetration. For samples treated with THPC-type reagents, Acid Blue I (CI #42045) dyes the reagent polymer but not the cotton. By cutting cross sections of yarn it is possible to see the dyed polymer between fibers and on fiber surfaces. Penetration into fibers can also be detected to some extent.

For more detailed study of reagent penetration, it is necessary to use the greater magnification and resolution available in the electron microscope. Ultrathin cross sections, 500 to 1,000 μm thick, of the treated fibers showed no structural change due to treatment. In solubility tests, cupriethylenediamine hydroxide dissolved fibers treated with THPOH-NH_3 just as it does untreated fibers. Cross sections of fibers treated with THPC-amide were not completely soluble, indicating that some cellulose cross-linking had probably protected the fiber from dissolution. Since solubility studies revealed little definite information on polymer penetration, microincineration of the sections was carried out.

Low-temperature incineration is a technique for combustion of organic materials at temperatures below 100° C by oxygen gas at low pressure, activated in a high-frequency electrical field. This type of burning reduces shrinkage and leaves ash residue deposited near its original position. Ultrathin sections of scoured and bleached fibers ashed in the low-temperature reactor showed only residual primary wall skeleton and occasional traces of secondary wall residue. Sections from fibers which had been well treated with the flame-retardant revealed a heavy deposit on the primary wall and a lacy skeleton structure throughout the original diameter of the fiber, indicating complete penetration by the flame-retardant polymer. The amount of this residue was not always the same from section to section but was always greater than in the untreated section.

Treated fabric surfaces studied with the scanning electron microscope (SEM) showed heavy deposits on fabric and fiber surfaces. The coating was uneven, but all fibers showed some polymer on their surfaces. The amount of polymer penetrating the yarn was determined by viewing yarn cross sections. Such observations generally showed that the polymer had bound together the fibers on the periphery of the yarn where the deposit is usually heavier. Toward the center of the yarn the fibers were loose, but deposits could be seen between them.

Durability of the finish with laundering was measured by testing after 1, 5, 20, and 50 laundry cycles. Most of the samples passed the standard vertical flame test even after 50 laundry cycles, but SEM observations indicated that after one laundry cycle, surface deposits had begun to break up. After five cycles much of the surface deposit had been removed, and fiber surfaces showed evidence of abrasion damage. Twenty and fifty laundry cycles almost completely removed surface deposits, and extensive abrasion damage was noted.

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The mechanism of flame retardancy can be better understood by studying chars of samples burned in the standard vertical flame test. After burning, the treated fabric retained its fibrous, woven appearance. The coating on and between the fibers appeared to be fused, forming bubbles in the polymer. Cross-sectional views at yarn ends indicated that fiber wall thickness had been reduced by as much as two-thirds, giving the fiber a hollow appearance. Groups of fibers were fused together by the melted chemical. Studies of the chars of laundered samples revealed that as the number of washing cycles on the original sample increased, the amount of surface bubbling on the char decreased. However, fused polymer was still present in some samples even after 50 launderings.

Microscopical testing is not meant to be a standard for measuring performance of flame retardants, but rather is a means of better understanding what happens to a fabric when it is given such a treatment, and what happens to the treated fabric when it is burned.

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